Electrical Properties of Niobium Based Oxides-Ceramics and Single Crystal Fibers Grown by the Laser-Heated Pedestal Growth (LHPG) Technique

A Thesis in
Materials

by
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ABSTRACT

Dielectric materials have been studied for decades due to both their application in important technologies and the fundamentally interesting relationships among their crystal chemistry, crystal structures, and physical properties. Recently, dramatic changes in microelectronics and in particular wireless communications technologies have made the importance of materials with the unusual combination of high dielectric constant, low dielectric loss, and low temperature dependence of dielectric constant of great interest.

Tantalum oxide is one of the interesting dielectric materials from a crystal chemical point of view, as the complexity of its crystal structure allows it to accommodate many different dopant ions in significant concentrations with only minor changes in its crystal structure. The dielectric constant of bulk Ta$_2$O$_5$ can be enhanced significantly through small substitutions of selected oxides such as TiO$_2$, or Al$_2$O$_3$. Some studies on the dielectric properties of the isostructural Nb$_2$O$_5$ have also been reported. It is desirable to investigate the dielectric behavior of both Ta$_2$O$_5$ and Nb$_2$O$_5$ compounds as those have potential as thin film dielectric in various devices.

This thesis is dedicated to gain understanding of the dielectric behavior of Niobium-based oxide ceramics and single crystals. The work presents the results on the Nb$_2$O$_5$ system in three specific areas:

(i) Unusual enhancement of dielectric constant of Nb$_2$O$_5$ has been observed through the small substituents such as TiO$_2$, SiO$_2$, and Al$_2$O$_3$. The ceramics of these solid solutions are prepared by the conventional mixed oxide method. Single crystal
fibers are grown by the Laser-Heated Pedestal Growth (LHPG) technique, which is considered to be a powerful tool for rapid growth of high-melting temperature oxides and incongruent melting compositions. Optimized growth parameters are established to obtain the best quality of single crystal fibers.

(ii) This work is the first report on the single crystal growth of the solid solution and the anisotropic dielectric behavior of the crystals. Interesting dielectric relaxation has been observed in these materials and analyzed by Arrhenius, Vogel-Fulcher, and Cole-Cole relationship. The direct-current (dc) electric field dependence of the dielectric constant has been studied. The results show the strong dielectric dispersion which exists in a large frequency range implies that the relaxation process involved is not of a simple Debye type. Nb_2O_5 system is known to have Magneli’s phases of the polar group symmetry. The large dielectric constants, the anisotropic behavior and the field dependence of the dielectric properties could be associated with the presence of polar clusters or the similar groups of Magneli’s phases in the solid solution compositions studied. The influence of the cluster size dispersion is one assumption. The data of dc bias field dependence of the dielectric constant has been analyzed by the modified Devonshire relation including a cluster term giving the fitted parameters: cluster sizes distribution and their polar cluster polarization.

(iii) The nanoscale distribution of Magneli’s phases also influences the thermal expansion behavior of the samples. The measurements are made on the solid-
solution Nb$_2$O$_5$- based oxide samples in the ceramics and single crystal in the temperature range of -200 to 500°C by using the dilatometer technique. Both single crystals and ceramics show negative thermal expansion in this temperature range. Nevertheless, the thermal expansion coefficient of these solid solutions can be designed to achieve a desired overall coefficient by either annealing or processing history.

In brief, the research is aimed to develop a good understanding of the dielectric behavior of ceramics and single crystals of these materials through the structure-property relationships. Various characteristics such as dielectric constant and losses, anisotropic dielectric properties of crystals, electric-field dependent dielectric properties, oxygen stoichiometry effect, analysis of relaxation behavior, negative thermal expansion coefficients, are investigated in both ceramic and single crystal fiber forms to judge the potential of these materials in electronic and fiber based applications. Studies also suggest that the presence of Magneli’s phases or polar clusters in these compositions has a direct association with the unusual properties observed in these materials.
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Chapter 1

THESIS STATEMENT

1.1 Introduction

The continuing drive toward device miniaturization suggests that the evaluation of new potential dielectric materials should be a fruitful area of research. Enhancement and optimization of dielectric properties is a most challenging topic of research. Dielectrics are required for advanced microelectronic applications. High permittivities are required, but not anywhere closer to a typical ferroelectric capacitors; permittivities of ~100 with lower losses would be a major advancement in a simple material system. This has been the challenge to the industry and research community for many years. Recently, enhancement in the permittivity of some of the classic dielectric systems has been studied. For example, the dielectric constant of Ta$_2$O$_5$ increased by a factor of 5 just by the addition of simple off-site cation substituents.\textsuperscript{1-3} Cava et al. (1995) have reported that the dielectric constant of tantalum oxide (Ta$_2$O$_5$) can be increased from 35.4 to 126.2 by adding in it about 8 mol % of titanium oxide (TiO$_2$). Their measurements were carried out on the (Ta$_2$O$_5$)$_{1-x}$: TiO$_2$$_x$ bulks that were prepared with a standard ceramic processing technique. Gang et al. (1998) observed the similar composition dependence of dielectric constant in thin (Ta$_2$O$_5$)$_{1-x}$: TiO$_2$$_x$ film that were fabricated at lower temperature. The highest dielectric constant measured in this work was about 55; that is
much lower than the value reported on bulks. Jiang, Guo and Bhalla reported the enhancement by a factor of 10 in their ceramic samples.\textsuperscript{4} 

Some studies on the isostructural Nb\textsubscript{2}O\textsubscript{5} also reports the high dielectric constants in this compound.\textsuperscript{5} For example, Nb\textsubscript{2}O\textsubscript{5} with the H-type structure, a stable form at high temperature and pressure, has a dielectric constant of about 100, considerably higher than that of SiO\textsubscript{2} or Ta\textsubscript{2}O\textsubscript{5}.\textsuperscript{6,7} Meanwhile, several investigators have studied niobium pentoxide, Nb\textsubscript{2}O\textsubscript{5}, as an electrically conductive material.\textsuperscript{8-13} Due to the fact that Nb\textsuperscript{5+} has the same valency as Ta\textsuperscript{5+}; the small addition of some oxides in Nb\textsubscript{2}O\textsubscript{5} has been expected to increase the dielectric constant of Nb\textsubscript{2}O\textsubscript{5} as well. But there are some reports contrary to that expectation.

Therefore, it will be of great interest to investigate the behavior of enhancements of dielectric constant of Nb\textsubscript{2}O\textsubscript{5} through various substituents such as TiO\textsubscript{2}, SiO\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3} in both ceramic and single-crystal forms. The laser-heated pedestal growth technique (LHPG) is considered to be a powerful tool for rapid growth of small diameter single crystals (particularly high-melting-temperature oxides and incongruent melting compositions) for both property studies and use in fiber devices.\textsuperscript{14,15}

1.2 Statement of Thesis Purpose

The main objective of this dissertation is to carry out the studies of dielectric properties of niobium based oxides and their solid solution and specifically to focus on the enhancement in dielectric properties through various substituents such as Ti, Si, Al in the classical dielectric systems. Our focus has been a basic study to identify the
mechanisms by which such substituents make substantial and important changes in their (classical dielectrics) electrical behavior. It is also our aim to develop a good understanding of the dielectric behavior of ceramics and single crystals of these materials through the structure-property relationships.

The specific targets are two fold: (1) Test the feasibility of single crystal fiber growth by utilizing the laser heated pedestal growth (LHPG) technique. (2) Evaluate and compare with ceramics the various characteristics of the fibers such as crystallographic parameters, thermal expansion coefficients, anisotropic dielectric properties, electric-field dependent dielectric properties, oxygen stoichiometry effect, and relaxation behaviors, to judge the potential of these materials in electronic application.

These goals will be accomplished by

1) Optimization of the growth parameters to obtain the good quality of niobate-based oxide single crystal fibers.
2) Investigating the dielectric properties of these materials in the bulk ceramic and single crystal fiber forms.
3) Examining the influence of composition variation and dopant type.
4) Examining the anisotropic crystal properties.
5) Investigating the effect of temperature, frequency, electric field dependent, and oxygen history dependent dielectric properties.
6) Investigating the effects of Magneli’s phases which generally occur in the Nb$_2$O$_5$ system.
By achieving the above goals, the results would provide the fundamental understanding of the dielectric behavior of these solid solution systems, which have the potential in electronic devices and various fiber based applications.

1.3 Organization of the Thesis

This thesis is organized according to the sequence of objective described above. It includes of 7 main chapters.

Chapter 2 provides the background needed for the research areas covered in the following chapters. Three major knowledge and literature reviews used in this thesis framework were presented in the following sequences; (1) dielectric in solid materials, (2) pure substance Nb$_2$O$_5$ properties, and (3) laser-heated pedestal growth (LHPG) technique. The subject of dielectrics is so rich in content and so varied in scope, and the resulting literature is so voluminous, that it is essential to define clearly the scope of the present work. First part, dielectric in solid materials, guides the readers through the phenomenon of dielectric polarization, how to measure the dielectric properties in materials, thereby introducing the concept of frequency dependences of the dielectric permittivity and loss or dielectric relaxation phenomena including various models that were proposed to study the relaxation mechanism. The next part is intended to study the nature of Nb$_2$O$_5$ which was aimed as a main material in this research. The last part is the introduction of the single crystal growth by the Laser-Heated Pedestal Growth (LHPG) technique which was employed to grow the single crystal specimens for this research.
In Chapter 3, an overall description of specimen processing is described by dividing into 2 categories; ceramic processing and the preparation of single crystal. The processing parameters and the characterization of each ceramic are reported. The single crystal growth conditions of each composition and their characterizations are also presented.

Chapter 4 is dedicated to the investigation of dielectric properties. The scope of measurement is defined and the results of dielectric permittivity and dielectric loss are shown. The dielectric measurements are first made on the pure Nb₂O₅ ceramics and single crystals following the measurements in other compositions to study the effect of substituents. The effect of external environments such as oxygen annealing, applied bias field is studied as well. Most dielectric characteristics of these solid-solutions suggest the presence of interesting dielectric relaxation phenomena in these samples. Therefore, several models are viewed to analyze the relaxation mechanism.

Chapter 5 is intended to investigate the existing of polar-cluster nanoregions in single crystals of Nb₂O₅ based oxides due to the fact that these oxides depict the high dielectric constant and strong nonlinear dielectric response to the external electric field. It is assumed that the presence of polar clusters causes the high dielectric constant and the distribution of cluster sizes along with defect dipoles generates the relaxation in these samples.

Chapter 6, the thermal expansion behavior of Nb₂O₅-based oxides solid solutions and its possible association with the Magneli’s phases are presented.

Finally, in Chapter 7, the overall conclusions of this study are drawn and the future extensions of this study are proposed.
1.4 References

Chapter 2

BACKGROUNDs AND LITERATURE REVIEWS

In this chapter, the fundamental knowledge which is used in this thesis has been described including the dielectric properties in solid materials, the characteristics of dielectric relaxation, the unique structure of pure Nb$_2$O$_5$ and its polymorphism. A short description of the principle of the Laser-Heated Pedestal Growth (LHPG) technique which is employed to grow the single crystal fibers is also provided in this chapter for better understanding and seeing the advantages of this technique.

2.1 Introduction

Enhancement and tailoring of dielectric properties of a material is a most challenging topic of research. Dielectrics are required for advanced microelectronic applications. High permittivities are required for various thin film circuits and microwave applications, but not anywhere closer to a typical capacitor ferroelectrics; permittivities of ~100 with lower losses would be a major advancement in a simple materials system. This has been the challenge to the industry and research community for many years. Recently, enhancements in the permittivity of some of the classic dielectric systems have been achieved. For example, the dielectric constant of Ta$_2$O$_5$ has been increased by a factor of 5 just by simple off-site cation substituents.$^{1-3}$ Cava et al. (1995) have reported that the dielectric constant of tantalum oxide (Ta$_2$O$_5$) can be increased from 35.4 to 126.2 by
adding about 8 mol % of titanium oxide (TiO$_2$). Their measurements were carried out on the (Ta$_2$O$_5$)$_{(1-x)}$: TiO$_2$(x) bulks that were prepared with a standard ceramic processing technique. Gang et al. (1998) observed the similar composition dependence of dielectric constant in thin (Ta$_2$O$_5$)$_{(1-x)}$: TiO$_2$(x) film that are fabricated at lower temperature. The highest dielectric constant measured in this work is about 55; that is much less than the value reported on bulks. Jiang, Guo and Bhalla reported the enhancement by a factor of 10 in their ceramic samples and single crystals.$^4$

It has been reported that Nb$_2$O$_5$ exhibit high dielectric constants compared to those of other oxide material.$^5$ For example, Nb$_2$O$_5$ with the H-type structure, a stable form at high temperature and pressure, has a dielectric constant of about 100, considerably higher than that of SiO$_2$ or Ta$_2$O$_5$.$^6,7$ Meanwhile, several investigators have also studied niobium pentoxide, Nb$_2$O$_5$, as an electrically conductive material.$^8-13$ Due to the fact that Nb$^{+5}$ has the same valency as Ta$^{+5}$; the small addition of some oxides in Nb$_2$O$_5$ has been expected to increase the dielectric constant of Nb$_2$O$_5$ as well. But there are some reports contrary to that expectation.

Therefore, it will be of great interest to investigate the behavior of enhancements of dielectric constant of Nb$_2$O$_5$ through various substituents such as TiO$_2$, SiO$_2$, and Al$_2$O$_3$ in both ceramic and single-crystal forms. The laser-heated pedestal growth technique (LHPG) is considered to be a powerful tool for rapid growth of small diameter single crystals (particularly high-melting-temperature oxides and incongruent melting compositions) for both property studies and use in fiber devices.$^{14,15}$
2.2 Dielectric in Solid Materials

2.2.1 Preliminary Considerations

Charges, Dipoles, and Chemical Bonds

At the atomic level, all matter consists ultimately of positive and negative charges balancing each other microscopically or macroscopically: the former corresponding to overall charge neutrality, the latter giving rise to local space charge, but even in that condition one expects to find the net charge over a given volume or sample to be zero. Even though the positive and negative charges do not separate completely in space to give two separate free particles of opposite sign, the charge distribution within a neutral molecule may be distorted to create a local molecular charge imbalance in which the "centres of gravity" or the first moments of the positive and negative charges, ±q, become separated by a finite distance d, thus creating a dipole with a dipole moment \( \mu = qd \).

The case of fixed d corresponds to situation in which the charge separation is caused by chemical interactions between dissimilar atoms constituting the molecule, e.g. HCl, where the different electron affinities of the atom give rise to the appearance of net charges on each atom, in this instance H\(^+\)—Cl\(^-\). The situation leads to the creation of a permanent dipole whose dipole moment is dominated by the strong intramolecular interactions and is not seriously affected by external factors such as electric field and temperature. The other type of dipole arises in atoms or molecules in which no significant charge separation occurs as a result of chemical interactions and in which the separation takes place between the outer valence electrons and the atomic cores. In these cases we
assume that the dipole moment is proportional to the electric field according to the relation \( \mu = \alpha E \), where \( \alpha \) is the polarisability of the molecule.

The formation of permanent dipoles and the polarisability of molecules are very intimately linked with the nature of the chemical bonds between atoms in molecules.\(^2\) In non-metallic solids these bonds may be covalent or ionic, respectively to the limit of negligible charge transfer and of complete charge transfer between atoms. Thus, a diatomic molecule consisting of identical atoms, e.g. H\(_2\) or N\(_2\) must necessarily be covalently bonded since symmetry precludes any charge transfer. The corresponding situation arises in non-metallic elemental crystal, e.g. silicon or diamond, where the bonds are completely covalent. Classic examples of completely ionic bonds are to be found in solids, such as the alkali halides NaCl, KCl, etc. where the charge transfer between the positive cations Na\(^+\) and the negative anions Cl\(^-\) is complete, leading to the formation of completed valence shells in both species. The bonding forces in such solids are predominantly the Coulomb attraction between oppositely charged nearest neighbors, balanced by the strong repulsion as ions approach more closely than is allowed by their effective ionic radii.

All compound solids consisting of dissimilar atoms, e.g. ZnS, SiO\(_2\), BN, have partially covalent and partially ionic bonds, in which the charge transfer is finite but not sufficient to produce completed outer valence shells in the constituent ions.\(^3\) In addition to the induced polarisability of the individual ions, ionic solids are also polarisable by virtue of the relative shifts of the positive and negative sub-lattices from their equilibrium positions.
Electrical Phenomena

Capacitance: The electrical engineer is most concerned with dielectric materials in relation to a capacitor in an electrical circuit. The principal characteristic of a capacitor is that an electrical charge $Q$ can be stored. The charge on a capacitor is

$$Q = CV$$  \hspace{1cm} (2.1)$$
where $V$ is the applied voltage and $C$ is the capacitance. The voltage is directly proportional to the amount of charge stored, and the current passing through the capacitor is given by

$$V = \frac{Q}{C} = \frac{\int Idt}{C}, I = C \frac{dV}{dt}$$  \hspace{1cm} (2.2)$$

With a sinusoidal voltage

$$V = V_0 \exp i \omega t$$  \hspace{1cm} (2.3)$$
As used in ac circuits, a charging current results

$$I_c = i \omega CV$$  \hspace{1cm} (2.4)$$
leading the voltage by a temporal phase angle of $90^\circ$; $i$ equals $\sqrt{-1}$ and $\omega$ equals $2\pi f$, where $f$ is the frequency in cycles per second.

The capacitance $C$ contains both a geometrical and a material factor. If a material of permittivity $\varepsilon'$ is inserted between the capacitor condensers,

$$C = C_0 \frac{\varepsilon'}{\varepsilon_0} = C_0 \kappa'$$  \hspace{1cm} (2.5)$$
where $\varepsilon'$ and $\varepsilon_0$ designate the real permittivities or dielectric constants of the dielectric and of vacuum, respectively, and their ratio $\kappa'$ the relative dielectric constant of the material.
**Polarization:** A dielectric material reacts to an electric field differently from a free space because it contains charge carriers that can be displaced, and charge displacements within the dielectric can neutralize a part of the applied field. Some charges can drift through the material to be discharged at the electrodes, while other charges are bound and can only oscillate to produce a polarization. The total electric displacement $D$ (also called the electric flux density) is a measure of the sum of current flow from the shifting charge and can be related to the electric field through the permittivity of the material by

$$D = \varepsilon' E = \varepsilon_0 E + P$$

(2.6)

where $P$ is the resultant polarization or surface charge density of the material caused by the bound charges. **Figure 2-1** schematically represents the dielectric polarization by dipole chains and bound charges of the dielectric material.
Figure 2.1: Schematic representation of dielectric polarization.
The polarization $P$ can also be related to the dipole moment per unit volume of the material, summed over all the types of dipole (i) by:

$$P = \sum_i N_i \mu_i$$  \hspace{1cm} (2.7)

where $N$ is the number of dipoles per unit volume and $\mu$ is the dipole moment relating two opposite charge ($\pm q$) separated by a distance $d$ by $\mu = qd$. Thus polarization can equivalently designate either the bound-charge density or the dipole moment per unit volume. From Eqn. 2.6,

$$P = \varepsilon' E - \varepsilon_0 E = \varepsilon_0 (\kappa' - 1) E$$  \hspace{1cm} (2.8)

Another measure of the ratio of polarization to applied field is the electrical susceptibility:

$$\chi = \kappa' - 1 = \frac{P}{\varepsilon_0 E}$$  \hspace{1cm} (2.9)

The susceptibility is the ratio of the bound charge density to the free charge density.

**Loss Factor:** The dielectric loss relates the polarization and current in an alternating field. The time required for polarization is reflected as a phase retardation of the charging current. Instead of being $90^\circ$ advanced of the voltage, the current is advanced by some angle $90 - \delta$, with difference generally referred to as the loss angle ($\delta$). Representing the electric field and displacement (flux density) in complex notation:

$$E = E_0 e^{i\omega t}$$  \hspace{1cm} (2.10)

$$D = D_0 e^{i(\omega t - \delta)}$$  \hspace{1cm} (2.11)

And making use of the relation

$$D = \kappa^* E$$  \hspace{1cm} (2.12)

One obtains
\[ \kappa^* = \kappa_\epsilon e^{-i\delta} = \kappa_\epsilon (\cos \delta - i \sin \delta) \quad (2.13) \]

where \( \kappa_\epsilon = D_0 / E_0 \) is the static dielectric constant. In term of a complex dielectric constant

\[ \kappa^* = \kappa' - i\kappa'' = \frac{\varepsilon^*}{\varepsilon_0} = \frac{1}{\varepsilon_0} (\varepsilon' - i\varepsilon'') \quad (2.14) \]

One has from Eqn. 2.13

\[ \kappa' = \kappa_\epsilon \cos \delta \quad (2.15) \]
\[ \kappa'' = \kappa_\epsilon \sin \delta \quad (2.16) \]

The loss tangent can then be defined as the ratio of Eqn. 2.15 and 2.16

\[ \tan \delta = \frac{\kappa''}{\kappa'} = \frac{\varepsilon''}{\varepsilon'} \quad (2.17) \]

Alternatively, \( \tan \delta \) is also known as the dissipation factor (D). The inverse of \( \tan \delta \) is commonly used as a figure of merit known as the quality factor (Q).

**Molecular Mechanism of Polarization**

The polarization \( P \) created in a dielectric material on a macroscopic level by an external electric field is related to the molecular level through the equivalent to the dipole moment per unit volume of the material (Eqn. 2.7). The local dipole moment (\( \mu \)) can be related to the local electric field strength \( E' \) by

\[ \mu = \alpha E' \quad (2.18) \]

The proportionality factor \( \alpha \), called polarizability, measures the electrical pliability of the particle, that is, the dipole moment per unit field strength. Eqn. 2.8 gives us the two alternative expressions for the polarization.
liking the macroscopically measured permittivity to molecular parameters: The number of contributing elementary particles per unit volume $N$; their polarizability $\alpha$; and the locally acting electric field $E'$. This field will differ from the applied field $E$, due to the polarization of the surrounding dielectric medium. It is important to understand the various polarization phenomena that generate the sum of contributions to the polarization of a dielectric material:\(^8\)

a) Electronic polarizability ($\alpha_e$) is due to the displacement of the negatively charge electron with respect to the positively charge nuclei in response to an external electric field; induced dipole moments result and cause the so-called electronic polarization of materials.

b) Ionic polarizability ($\alpha_i$) is the result of asymmetric sharing of electrons from atoms of different types form molecules as the electron clouds will be displaced eccentrically toward the stronger binding atoms.

c) Dipole polarizability ($\alpha_d$) or orientation polarizability is related to the asymmetric charge distribution between the unlike partners of a molecule giving rise to permanent dipole moments which exist also in the absence of an external field. Such moments experience a torque in an applied field that tends to orient them in the field direction.

d) Space charge polarizability ($\alpha_s$) is due to the mobile charges which are present because they are impeded by interfaces, because they are not supplied at an electrode or discharged at an electrode, or because they are trapped in the
material. Space charges resulting from these phenomena appear as an increase in capacitance as far as the exterior circuit is concerned.

The total polarizability of the dielectric can be represented as the sum of these:

$$\alpha = \alpha_e + \alpha_i + \alpha_d + \alpha_s$$

(2.20)

It is the response of these polarization mechanisms to periodic fields that determine the frequency dependence of the dielectric properties of solid. For each polarization mechanism, there exists some sufficiently high frequency such that the particular mechanism will not be able to follow the alternating field and thus will cease the contribution to the polarization and dielectric properties. In an ideal capacitor the electric charge adjusts itself instantaneously to any change in voltage. In practice, however, there is an inertia-to-charge movement that shows up as a relaxation time for charge transport. The electronic polarization is the only process sufficiently rapid to follow alternative fields in the visible part of the spectrum. Ionic polarization process is able to follow an applied high-frequency field and contribute to the dielectric constant at frequencies up to the infrared region of the spectrum.

2.2.2 Presentation of Dielectric Functions

Measurements for dielectric responses are carried out almost exclusively on samples in the form of two terminal devices consisting of two metallic or otherwise conducting plates with the dielectric medium filling the space between these plates. Figure 2-2(a) shows a rather arbitrarily shaped block of dielectric material with two conducting areas of equally arbitrary shape and area. We may now define the capacitance
of this device in terms of the ratio of the charge $Q$ induced on the plates to the voltage $V$ applied between the plates:

$$C = \frac{dQ}{dV}$$  \hspace{1cm} (2.21)

This definition is completely general, regardless of the geometry of the device used and is independent of the homogeneity and linearity of the material under investigation.

Although irregularly shaped samples such as those shown in Figure 2-2(a) may sometimes be used, it is far more convenient and advisable to use samples of well defined geometry, such as the parallel-plate structure shown in diagram b), with two plates of area $A$ adjacent to a planar slab of thickness $w$, so that fringing effects may be neglected. These arise because the field is only well defined in the area well removed from the edges and therefore quantitative deductions about the value of the permittivity and loss can only be made on samples in which these fringing fields are negligible. Subject to the stipulation that $A \gg w^2$, assuming that the dielectric material between the plates is homogeneous and that the electrodes make an intimate contact with this material, and also that the material has a linear response with respect to the amplitude of the applied voltage, we may write the expression for the electric field $E = \frac{V}{w}$, the total charge is given by $Q = AL$, where $L$ is the charge density per unit area of the plate. Making use of the fact that the dielectric induction $D$ represents the total charge density induced on the electrodes by a field $E$, we may write

$$Q = AL = AD = A\varepsilon E = \frac{\varepsilon AV}{w}$$  \hspace{1cm} (2.22)

which with equation (2.1) gives the expression for the capacitance:

$$C = \frac{\varepsilon A}{w}$$  \hspace{1cm} (2.23)
In this manner, a measurement of the capacitance which is readily performed in terms of the measurement of the physical quantities of charge and voltage, leads directly to the determination of the dielectric permittivity. If the applied voltage is a steady voltage \( V_o \), the capacitance so obtained is the steady state capacitance \( C_s \). If, on the other hand, the applied voltage is an alternating signal at a frequency \( \omega \), then the measured capacitance is a complex quantity whose real and imaginary parts correspond directly to the real and imaginary components of the complex permittivity:

\[
C(\omega) = C'(\omega) - iC''(\omega) = \left( \frac{A}{w} \right) \{ \varepsilon'(\omega) - i\varepsilon''(\omega) \}
\] (2.24)

\( C'(\omega) \) corresponds to the ordinary capacitance, while the imaginary component \( C''(\omega) \) represents the dielectric loss component. It is customary to define the loss angle \( \delta \) by which the phase of the induction \( D(\omega) \) lags behind the driving voltage \( E(\omega) \). The tangent of this loss angle is given by the relation:

\[
\tan \delta = \frac{\varepsilon''(\omega)}{C'(\omega)} \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}
\] (2.25)

It is convenient to define the geometrical capacitance of a capacitor in terms of the value of capacitance that would be obtained with the same geometry but with the dielectric medium being replaced by free space (vacuum):

\[
C_0 = \frac{\varepsilon_0 A}{w}
\] (2.26)

So that the ratio of the measured capacitance to the geometrical capacitance gives the ratio of the true complex permittivity to the permittivity of free space, known as the relative dielectric permittivity:

\[
\varepsilon_r(\omega) = \frac{C(\omega)}{C_0} \frac{\varepsilon(\omega)}{\varepsilon_0}
\] (2.27)

The real part of which is known as the dielectric constant \( K \).
Figure 2-2: Capacitor structures. Diagram a) an arbitrarily shaped dielectric body with two metallic electrodes partially covering opposite faces, b) regular planar geometry of thickness $w$ and with a guard electrode $G$ surrounding the surface electrode of area $A$. 
2.2.3 Dielectric relaxation

2.2.3.1 Introduction

Dielectric relaxation in ceramics occurs at various frequencies, depending on the type of chemical or physical defects. These defects depend on either intrinsic or extrinsic heterogeneities due to special heat treatments (quenching, annealing,…), ionic substitutions, grain size additives, and grain boundary nature. Defects may cause modifications of the short and/or long-range interactions in inorganic ceramics. Dielectric properties are generally very sensitive to both external (temperature, electric field, ionic substitutions,…) and intrinsic (defect, domain configuration,…) modifications because the polarization is largely affected. For example, an ideal ferroelectric should be a good electrical insulator, as it kept its spontaneous polarization, i.e. its electric charge.\textsuperscript{10} In fact, such a property depends on external stresses such as the temperature and the applied electric field frequency, i.e. the decrease in $P_s$ with temperature and its cancellation at Curie temperature $T_C$. There is more complex reason for the decrease of insulating properties. When an alternating current is applied to a sample, the dipoles responsible for the polarization are no longer able to follow the oscillations of the electric field at certain frequencies. The field reversal and the dipole reorientation become out-of-phase, giving rise to energy dissipation. Such an effect is called dielectric relaxation.\textsuperscript{11}
2.2.3.2 Relaxation Phenomena

In an ideal capacitor the electric charge adjusts itself instantaneously to any change in voltage. In practice, however, there is an inertia-to-charge movement that shows up as a relaxation time for charge transport. This is exactly analogous to the time required for elastic strain to follow an applied stress. A dielectric relaxation phenomenon reflects the delay (time dependence) in the frequency response of a group of dipoles submitted to an external applied field. Because the polarization vector cannot always follow the variation of the alternating field, the frequency response is expressed in terms of the complex dielectric permittivity $\varepsilon^*$:¹

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$  \hspace{1cm} (2.28)

where $\omega = 2\pi f$ is the angular frequency; $f$ is the circular frequency (Hz) of the oscillating field and $i$ a complex number ($i = \sqrt{-1}$). The real ($\varepsilon'$; component in phase with the field) and imaginary ($\varepsilon''$; component in quadrature) parts of the permittivity are dependent on each other as shown by the Kramer-Kronig relations:

$$\varepsilon'(\omega) - \varepsilon_\infty = 2 / \pi \int_0^\infty \frac{\varepsilon''(\omega')}{(\omega')^2 - \omega^2} \omega' d\omega'$$  \hspace{1cm} (2.29)

$$\varepsilon''(\omega) = 2 / \pi \int_0^\infty (\varepsilon'(\omega') - \varepsilon_\infty) \frac{\omega}{(\omega')^3 - \omega^3} d\omega'$$  \hspace{1cm} (2.30)

Where $\omega'$ is an integration variable and $\varepsilon_\infty$ is the high frequency dielectric constant.

Such relations evidence the correlation between dispersion (variation of $\varepsilon'$ as a function of frequency) and absorption (non-zero value of $\varepsilon''$): any dielectric dispersion is accomplished by an absorption peak. $\varepsilon'$ is correlated with the polarization of the system; $\varepsilon''$ with the energy losses.
Over a wide frequency range, different types of polarization cause several dispersion regions (Fig. 2-3). The critical frequency, characteristic of each contributing mechanism, depends on the nature of dipoles. When the frequency increases, the number of mechanisms involves in the dynamic polarization decreases. At very high frequency, only the electronic contribution of the polarization remains. A decrease of $\varepsilon'$ is observed with decreasing frequency. Each polarization mechanism is characterized by a critical frequency $f_r$ (relaxation frequency) corresponding to the maximal phase shift between the polarization $P$ and the applied electric field $E$; a maximum of dielectric loss ($\tan \delta = \varepsilon'' / \varepsilon'$ is the loss factor) occurs. The orientation polarizations, i.e. interfacial polarization (space charges) and dipole polarization, are observed from low to microwave frequencies. The force opposed to the motion is here of a frictional nature and the resulting dynamics are thus of the relaxation type. The deformation polarizations, i.e. ionic (oscillation of ions) and electronic polarizations (displacement of electrons with respect to the nuclei), are detected in short microwave and infrared ranges. The latter mechanisms lead to resonance-type dielectric dispersions (vibrational process, harmonic oscillator type).
Figure 2-3: Schematic representation of various relaxation and resonance type, $f$/Hz
2.2.3.3 Relaxation with a Single Relaxation time

The concept of dipole giving rise to polarization was introduced by Debye. The Debye model considers the reorientation of non-interacting dipoles in a purely viscous environment without an elastic restoring force. In terms of the dielectric constant \( \varepsilon_\infty \) corresponding to the instantaneous polarization \( P_\infty \) (the dielectric constant at frequencies much higher than \( 1/\tau \)), the complex dielectric constant may be expressed as

\[
\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}
\]  
(2.31)

Dividing this into real and imaginary parts gives:

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\tau)^2}
\]  
(2.32a)

\[
\varepsilon'' = \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\tau)^2} \omega\tau
\]  
(2.32b)

and

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\varepsilon_s + \varepsilon_\infty \omega^2 \tau^2}
\]  
(2.33)

where \( \tau \) is the relaxation time, \( \varepsilon_s \) is the permittivity at low frequency (\( f \ll \) relaxation frequency) and \( \varepsilon_\infty \) the one at high frequency (\( f \gg \) relaxation frequency). Equations 2.31 to 2.33 are often termed Debye equations. The Debye curves for dielectric dispersion \( \varepsilon' \) and absorption \( \varepsilon'' \) are symmetric about \( \omega\tau = 1 \). \( \varepsilon' \) decreases to \( \varepsilon_\infty \) with increasing frequency and \( \varepsilon'' \) is maximal at the frequency \( \omega = 1/\tau \). The frequency dependence of \( \varepsilon' \) and \( \varepsilon'' \) have been illustrated by the curves for \( K' \) and \( K'' \) in Fig. 2-4.

The Debye equations are based on the assumption that the transient polarization can be represented by a simple exponential with a single relaxation time. Hence any model which predicts a simple exponential rise of polarization on applying a field within...
an ac field lead to dielectric dispersion and absorption curves of the form given by Eqn. 2.12 and 2.13. For most materials, however, the experimental data are not well described by the Debye equations. Rather, the dispersion of the dielectric constant occurs over a wide range of frequency, and the absorption curves are much broader and flatter than shown in Fig. 2-4.
Figure 2-4: Frequency dependences of $\varepsilon'$ and $\varepsilon''$ and an Argand diagram: Debye model.
In the case of dipoles correlated through ferroelectric-type interactions, it is possible to translate the thermal vibration of permittivity at various frequencies (suitable to characterize the transition and given classically) into frequency dielectric dispersion curves at fixed temperatures. Argand diagrams (\(\varepsilon''\) versus \(\varepsilon'\) or \(K''\) versus \(K'\)) are also sometimes used for relaxation studies instead of the temperature and frequency variations of \(\varepsilon'\) and \(\varepsilon''\). The corresponding curves are of course related to each other (Fig. 2-4). The obtained curve is a semi-circle centered on the abscissa axis at the \((\varepsilon_s - \varepsilon_\infty)/2\) point.

Two parameters are characteristic of the Debye relaxation: the relaxation step \(\Delta\varepsilon' = \varepsilon_s - \varepsilon_\infty\) and the relaxation time \(\tau\). The dielectric dispersion \(\Delta\varepsilon'\) is then obtained by extrapolating at very low frequency \((f \ll f_s)\) for \(\varepsilon_s\) and at infinite frequency \((f \gg f_s)\) for \(\varepsilon_\infty\). Such parameters are related to the dipole characteristics: \(\Delta\varepsilon'\) is related to both the microscopic dipolar moment \(\mu\) and the number \(N\) of relaxing dipoles through the Langevin relation:

\[
\varepsilon_s - \varepsilon_\infty \approx \frac{N|\mu|^2}{3kT} \quad (2.34)
\]

\(k\) is the Boltzmann constant \((k=8.314 \times 10^{-5} \text{ eV K}^{-1})\).

The value of relaxation time \(\tau\) in the Debye equation is correlated to the energy barrier \(\Delta E\) separating the two minima corresponding to the two equivalent positions of the non-interacting dipoles in a double-well potential (viscous interaction between the dipole and the environment). Sometimes \(\Delta E\) is called the activation energy. The variation of the relaxation time maybe expressed as a thermally activated process through the Arrhenius relationship:
\[ \tau = \tau_o \exp\left(\frac{E_a}{kT}\right) \]  

(2.35)

where \( \tau \) is the time constant of the relaxation mechanisms (or the reciprocal of the measurement frequency in angular unit) ; \( \tau_o \) is the pre-exponential factor (and is related to the nature of mechanism responsible for relaxation phenomenon) ; \( E_a \) is the activation energy of the relaxation mechanism ; \( k \) is Boltzmann’s constant.

A thermally activated relaxation which is governed by the Arrhenius relationship is known as a Debye process. It predicts that the temperature of the absorption maximum should linearly decrease with decreasing decades of frequency; an additional requirement is that the shape of the absorption curve should not change. To investigate a Debye type-process it is only necessary to measure the dynamical response as a function of temperature, since the frequency dependence is a direct reflection of the temperature.

### 2.2.3.4 Distribution of Relaxation Times

The actual dispersion behavior observed in most dielectric solids is usually quite different than that predicted by the Debye equations. The \( \varepsilon''(\omega) \) peaks are broader and do not reach the expected magnitude, and the dispersion of \( \varepsilon'(\omega) \) occurs over a wider frequency range than expected. These differences from single-relaxation-time behavior are generally associated with the fact in condensed phases the environments of different ions are not all identical. Even in crystals, the magnitudes of the interactions between ions and of the thermal fluctuations are not identical for all places and all times. Hence it seems reasonable that a spread of relaxation times, distributed about the most probable relaxation time, is observed in experiments.
2.2.3.5 Cole-Cole analysis

The evaluation of experimental data is much facilitated by certain graphical methods of display, which permit the derivation of parameters by geometrical construction. The earliest and most used of these methods consists of plotting $\varepsilon''(\omega)$ for a certain frequency against $\varepsilon'(\omega)$ at the same frequency, in cartesian coordinates or in the complex plane. This diagram may be called the complex locust diagram or Argand diagram and was applied to dielectrics by Cole and Cole. It is often called the Cole-Cole plot or arc plot.

For a dielectric with a single relaxation time the Cole-Cole plot is a semi-circle. A simple evaluation of the Debye equations (2.31) and (2.32) shows that the equation between the real and imaginary part of the dielectric constant is the equation of a circle

$$\left(\varepsilon'(\omega) - \frac{\varepsilon_s + \varepsilon_\infty}{2}\right)^2 + \left(\varepsilon''(\omega)\right)^2 = \frac{1}{4}\left(\varepsilon_s - \varepsilon_\infty\right)^2 \quad (2.36)$$

The Cole-Cole plot therefore provides an elegant method of finding out whether a system has a single relaxation time. This plot is also useful for the characterization of different types of distribution function, and is widely applied.

The plot in Fig.2-5(a) can be considered in Cartesian coordinates but its treatment is mathematically more elegant in the complex plane. A point on the semi-circle defines two vector $u$ and $v$ as shown. By virtue of the construction

$$u - v = \varepsilon_s - \varepsilon_\infty \quad (2.37)$$

while

$$u = \varepsilon'(\omega) - \varepsilon_\infty + i\varepsilon''(\omega) \quad (2.38)$$

by definition. If the Debye equations apply
$$\nu = u \cdot \omega \tau$$  \hspace{1cm} (2.39)

which signifies that the two vectors are at right angles to each other, since multiplication by \(i\) signifies rotation by \(\pi/2\) in the complex plane.
Figure 2-5: (a) Arc plot for a Debye dielectric; (b) Arc plot for a dielectric with a Cole-Cole distribution characterized by the parameter $\alpha$. 
Cole and Cole generalize the representation of a Debye dielectric by a circular arc plot in the complex plane so that it applies to a certain type of distributions of relaxation times. They retain the vectors $u$ and $v$ and equations (2.37) and (2.38) but demand that $\varepsilon^*(\omega)$ should be so defined that

$$
\varepsilon^*(\omega) = \varepsilon_\infty \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}
$$

(2.41)

where $\tau$ and $\alpha$ are constants. The geometrical representation of this assumption is shown in Fig. 2-5(b). For any point on the arc defined by plotting $\varepsilon''(\omega)$ as a function of $\varepsilon'(\omega)$ the angle between $u$ and $v$ is $(1-\alpha)\pi/2$. This is the case for two secants of a circle where the radii drawn from the center of the circle subtend an angle $\pi(1-\alpha)$ as shown, and the construction of the circle follows from the diagram. Deviation from Debye behavior results in a tilting of this arc with respect to $\varepsilon'(\omega)$ axis. The Debye equation modified by Cole and Cole is given by

$$
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}
$$

(2.40)

The tilt angle is defined as $\alpha\pi/2$, and the tilt parameter ($\alpha$) is related to the distribution of relaxation times. Another feature of the Cole-Cole analysis is that the distribution of relaxation time is solely dependent on the tilt parameter ($\alpha$) by the following equation:

$$
F(s)ds = \frac{1}{2\pi} \frac{\sin\alpha\pi}{\cosh(1-\alpha)s - \cos\alpha\pi}
$$

(2.42)

The tilt parameter determines the breadth of the distribution of relaxation times; as the tilt parameter becomes larger, the distribution broadens.
2.3 Pure Nb₂O₅ Properties

To understand the properties of solid-solutions based on niobium oxide (Nb₂O₅) which is the main material aimed for study in this thesis, the properties of Nb₂O₅ should be thoroughly reviewed. This section will review the valuable information including the polymorphism of Nb₂O₅ from many publications.

2.3.1 Polymorphism of Nb₂O₅

Niobium pentoxide crystallizes in several different modifications and each appears to have a structure of some complexity. A large volume of literature is available on the polymorphism of Nb₂O₅, and the existence of no less than 15 polymorphs have been reported.¹⁴⁻¹⁷ In 1941, Brauer¹⁸ reported that Nb₂O₅ exist in three crystalline modifications and exhibit the following transformations: amorphous to $\gamma$ at 500°C, $\gamma$ to $\beta$ at 1000°C, and $\beta$ to $\alpha$ at 1100°C. In 1951, Hahn¹⁹ published X-ray data for an unspecified form of Nb₂O₅. The pattern did not correspond to Brauer’s $\alpha$, $\beta$, or $\gamma$ forms. Subsequently, Schafer et al.²⁰ presented the results of a partial X-ray investigation of the Nb₂O₅ –Ta₂O₅ system that included a study of the polymorphism of Nb₂O₅. This work confirmed the $\alpha$, $\beta$, and $\gamma$ polymorphs reported by Brauer. However, the transformation temperatures differed significantly. Frevel and Rinn²¹ reported a $\delta$-form which was indexed on the basis of a pseudohexagonal unit cell. The $\delta$-form is apparently converted to the $\gamma$-phase at 700°C, a contradiction of Brauer’s results. However, work by Shafer and Roy (1958)²² which is the most definitive summary demonstrated the existence of four
stable polymorphs under conditions of high water vapor pressure and high temperature. An $\alpha$ phase is stable up to 380°C, $\beta$ from 380°C to 1050°C, $\gamma$ between 1050°C and 1285°C, and $\delta$ from 1285°C until melting occurs at 1465°C. As Schaefer et al. pointed out, it is generally agreed that all varieties transform rapidly at temperatures above 1100°C to monoclinic H-Nb$_2$O$_5$, the high-temperature form. Several workers$^{14,15,20}$ have independently verified that the transformation is irreversible and that the monoclinic form is the truly stable form. The H-Nb$_2$O$_5$ is an insulator in the stoichiometric composition, but it changes into an n-type semiconductor when slightly reduced or when doped to create extrinsic defects.$^{23}$ All phase transitions as mentioned above from various sources in the literatures are concluded in Table 2-1.
Table 2-1: Phase transitions of Nb$_2$O$_5$

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature</th>
<th>Phase Transitions</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brauer, 1941</td>
<td>500°C, 1000°C, 1100°C</td>
<td>Amorphous → γ → β → α</td>
<td></td>
</tr>
<tr>
<td>Frevel &amp; Rinn, 1955</td>
<td>700°C</td>
<td>δ (pseudohexagonal) → γ</td>
<td>A contradiction of Brauer’s result</td>
</tr>
<tr>
<td>Holtzberg, 1957</td>
<td>435°C, 830°C</td>
<td>Amorphous → γ → α (monoclinic)</td>
<td>None of the transformations was reversible α and β phases are identical</td>
</tr>
<tr>
<td>Shafer &amp; Roy, 1958</td>
<td>380°C, 1050°C, 1285°C</td>
<td>α → β → γ → δ</td>
<td>High water pressure condition</td>
</tr>
<tr>
<td></td>
<td>880°C</td>
<td>α → γ</td>
<td>Dry condition, long time, no involvement of β</td>
</tr>
<tr>
<td>Hibst &amp; Gruehn, 1978</td>
<td>200°C</td>
<td>Nb$<em>{22}$O$</em>{54}$ (Magneli phase) → Nb$_2$O$_5$ → complex rearrangement of blocks</td>
<td>In air Monotropic phase transitions occurred on further heating</td>
</tr>
<tr>
<td>Ota, 1986</td>
<td>300°C</td>
<td>Nb$<em>{22}$O$</em>{54}$ (Magneli phase) → Nb$_2$O$_5$</td>
<td>In air</td>
</tr>
</tbody>
</table>

*Each reference designates the letter for indicating phase in different ways*
2.3.2 Crystallographic Shear Structure of Nb$_2$O$_{5-\delta}$

Structurally the chemistry of Nb$_2$O$_5$ is more complex than any other binary transition metal oxide. Its structure can be derived from insulating 4$d^5$ Nb$_2$O$_5$ by removal of rows of oxygen atoms, introducing small amounts of 4$d^1$ niobium 4+. These structures are known as “crystallographic shear” structures. The reduced niobium oxides were studied extensively by crystallographers during the development of the understanding of crystallographic shear structures. For niobium oxide, many distinct long-range-ordered structures are known at compositions Nb$_2$O$_5$ (NbO$_{2.50}$), Nb$_{53}$O$_{132}$ (NbO$_{2.49}$), Nb$_{25}$O$_{62}$ (NbO$_{2.48}$), Nb$_{47}$O$_{116}$ (NbO$_{2.47}$), Nb$_{22}$O$_{54}$ (NbO$_{2.45}$), and Nb$_{12}$O$_{29}$ (NbO$_{2.42}$). There are five compounds called “homologous series,” “block structures,” or “Magneli phases,” i.e. Nb$_{12}$O$_{29}$, Nb$_{22}$O$_{54}$, Nb$_{47}$O$_{116}$, Nb$_{25}$O$_{62}$, and Nb$_{53}$O$_{132}$ in the composition range between NbO$_2$ and Nb$_{28}$O$_{70}$ (=H-Nb$_2$O$_5$), and each phase also has a nonstoichiometric range. For the highly charged transition-metal oxides, in which sixfold (or higher) metal-oxygen coordination is preferred, point oxygen defects are energetically unfavorable and a different mechanism is required to accommodate variability in oxygen stoichiometry. For these metal oxides with three-dimensional blocks of corner-shared MO$_6$ octahedra as the basic structural component, it is not possible to remove significant amounts of oxygen without causing a structural rearrangement in which the blocks are broken along a plane of shared corners. The block parts are then shifted to eliminate whole rows of oxygen atoms, forming a shear plane of now edge-shared octahedra. Such shear planes cannot form in a random fashion; rather they form long-range-ordered arrays along the edges of ReO$_3$-type blocks.
All of the NbO$_{2.5-\delta}$ structures can be derived by the joining of blocks of corner-shared NbO$_6$ octahedra of size $n \times m \times \infty$ along plane of shared edges, with in some instances, NbO$_4$ tetrahedra inserted to help fill space. The high-temperature form of insulating Nb$_2$O$_5$, for instance, is made by $3 \times 4 \times \infty$ and $3 \times 5 \times \infty$ blocks of NbO$_6$ octahedra, with some tetrahedra as shown in Fig. 2-6. Nb$_{12}$O$_{29}$, the last of the series, has $3 \times 4 \times \infty$ blocks of octahedra, without tetrahedra, as shown in Fig. 2-7. In the real crystal structures, the niobium-oxygen octahedra are irregular in bond-length and bond angle, characteristic, characteristic of ferroelectric like structural distortions. The more complex compounds, for example, with formulas Nb$_{53}$O$_{132}$ and Nb$_{47}$O$_{116}$, consist of long-range alternation, on the unit cell level, of the simpler block structures. Nb$_{47}$O$_{116}$, for instance, consists of a 1:1 perfectly ordered alternation of Nb$_{22}$O$_{54}$ and Nb$_{25}$O$_{62}$ (Fig. 2-8).

Because the crystallographic unit cells of the Nb$_2$O$_{5-\delta}$ crystallographic shear structures are large and of low symmetry, and the crystal structures are so strongly related, their powder x-ray diffraction patterns are complex and quite similar. Conclusive identification of the phases through powder x-ray diffraction therefore required careful analysis. The best diffraction peaks for phase identification are below 30° 2θ when Cu Kα radiation is employed. Figure 2-9 compares as examples the powder x-ray diffraction patterns for orthorhombic Nb$_{12}$O$_{29}$ and monoclinic Nb$_{22}$O$_{54}$. 
Figure 2-6: The idealized crystal structure of Nb₂O₅, NbO₆ octahedra are shown, as well as tetrahedrally coordinated Nb by closed or open circles. Bold octahedra are on a level ½ octahedron height above the background octahedra. The structure repeats infinitely perpendicular to the plane of the figure, to form long columns of corner-shared octahedra dressed by planes of edge-shared octahedra. The planes of edge-shared octahedral occur at the location in the structure where the bold and background octahedra meet, and extend perpendicular to the plane of the paper.
Figure 2-7: The idealized crystal structure of orthorhombic symmetry Nb$_{12}$O$_{29}$.
Figure 2-8: The idealized crystal structure of Nb_{47}O_{116}. It is an ordered unit cell scale intergrowth of the two simpler compound Nb_{25}O_{62} and Nb_{22}O_{54}. 
Figure 2-9: Characteristic portions of the powder x-ray diffraction patterns for Nb$_2$O$_{54}$ and Nb$_{12}$O$_{29}$, Cu $K\alpha$ radiation.
2.3.3 Crystal Structure of the High Temperature Form of Nb$_2$O$_5$

At least 15 crystallographic forms of stoichiometric Nb$_2$O$_5$ have been reported\cite{Reisman1970}, however, as Schaefer et al. point out, it is generally agreed that all varieties transform rapidly at temperatures above 1100°C to monoclinic H-Nb$_2$O$_5$, the high temperature form. Several workers\cite{Phillips1970,Rutledge1970} have verified independently that the transformation is irreversible and that the H-form is the truly stable form. The idealized structure is shown in Fig. 2-6. Twenty-seven of the Nb atoms are in octahedral coordination and one is in tetrahedral coordination. The structure contains ReO$_3$-type blocks of two different sizes. At one level these are three octahedra wide and five long, and are joined, by sharing edges on both sides, into slabs running right through the structure in two directions. The second kind of block, three octahedra by four, cements these together by additional edge sharing, and leaves tetrahedral holes partly, but symmetrically, filled with niobium atoms. This form of Nb$_2$O$_5$ is the member \( n=9 \) of a possible series of structural homologues Nb$_{3n+1}$O$_{8n-2}$. The earliest work by Gatehouse and Wadsley (1964)\cite{Gatehouse1964} had provided quite completed crystallographic data for high temperature form Nb$_2$O$_5$ as concluded in Table 2-2.
Table 2-2: Crystallographic data for Nb₂O₅

<table>
<thead>
<tr>
<th>System</th>
<th>Monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit-cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 21.16 Å, b = 3.822 Å, c = 19.35 Å; β = 119° 50'</td>
<td></td>
</tr>
<tr>
<td>Systematic reflexions</td>
<td>None</td>
</tr>
<tr>
<td>Possible space groups</td>
<td>P2, Pm, P2/m</td>
</tr>
<tr>
<td>Dₘ</td>
<td>4.55 g.cm⁻³</td>
</tr>
</tbody>
</table>

[After Gatehouse et al. (1964)]
2.3.4 Defects and Transport Properties

The departure of H-Nb$_2$O$_{5.6}$ from stoichiometry as a function of temperature and pressure has been extensively studied.$^{28-34}$ The earlier results at lower temperatures suggested that the defect concentrations varies as $p_{O_2}^{-1/2}$ near stoichiometry and at $p_{O_2}^{-1/6}$ at lower oxygen pressures. This can easily be explained with a point defect model as:

$$O_0 \leftrightarrow V_0 + \frac{1}{2}O_2(H_v)$$

$$V_0 \leftrightarrow V_0^* + e^-(\varepsilon_1)$$

$$V_0^* \leftrightarrow V_0^{**} + e^-(\varepsilon_2)$$

If the dominant defects are $V_0^*$ we expect \( [V_0^*] \propto p_{O_2}^{-1/4} \) and if the dominant defects are $V_0^{**}$ we expect $p_{O_2}^{-1/6}$ law. Analysis of the temperature variation of the stoichiometry from thermal measurements gives

$$H_v + \varepsilon_1 + \varepsilon_2$$

105.8 kcal mol$^{-1}$ [Marucco, 1974]

103 kcal mol$^{-1}$ [Kofstad, 1968]

At 1100$^\circ$C, a discontinuity in resistance was found$^{25}$ corresponding to the formation of a new phase.

This simple view of point defects extending over a substantial stoichiometric range has been strongly challenged.$^{24}$ Typical stoichiometry data are shown in Figs. 2-10 and 2-11 and at very high temperature a series of breaks in curve strongly support the idea that a significant number of quite distinct phases can form. Combined structural and
thermal experiments at 1000°C [Nimmo et al., 1972] reveal the following domains for NbO₅:

(1) \(2.500 \geq x \geq 2.495\). Only the single phase H-Nb₂O₅₋₅ found without any local rearrangement or extended Wadsley defects. It is probable that in this range point defect theory may be used.

(2) \(2.495 > x \geq 2.480\). Two phases found corresponding to H-Nb₂O₅ and Nb₂₅O₆₂.

(3) \(2.480 > x \geq 2.417\). Two phases found corresponding to Nb₂₅O₆₂ and Nb₁₂O₂₉ (monoclinic).

Thus, at 1000°C, the reduction traverses the route H-Nb₂₈O₇₀ → Nb₂₅O₆₂ → Nb₁₂O₂₉. The structural relationship between these three phases is shown in Fig. 2-12. At higher temperatures, a quite different type of behavior is observed. In addition to the definite phases Nb₂₈O₇₀ (i.e. H-Nb₂O₅) and Nb₂₅O₆₂, a phase formed as an intergrowth, Nb₅₃O₁₃₂. The process of intergrowth is shown schematically in Fig. 2-13, which shows the regular intergrowth phase Nb₅₃O₁₃₂ as a natural intermediate. A similar intergrowth, Nb₄₇O₁₁₆, forms between Nb₂₅O₆₂ and Nb₁₂O₂₉ (Fig. 2-13). The reduction sequence at high temperature is then Nb₂₈O₇₀ → Nb₅₃O₁₃₂ → Nb₂₅O₆₂ → Nb₄₇O₁₁₆ → Nb₂₃O₅₄ → Nb₁₂O₂₉.
Figure 2-10: NbO$_x$. Composition parameter x vs. oxygen pressure. Solid lines: [Nimmo et al., 1972]; full and open circles: [Blumenthal et al., 1965]; dashed lines: [Kofstad et al., 1962]; triangle: [Abbatista et al., 1968]; 1300°C isotherm [Schafer et al., 1969]. Fig. from [Nimmo et al., 1972].
Figure 2-11: NbO$_x$. Oxygen partial pressure vs. composition at 1300°C and 1400°C [Kikuchi et al., 1976].
Figure 2-12: Structural relationship between (a) Nb$_{12}$O$_{29}$, (b) Nb$_{25}$O$_{62}$, (c) H-Nb$_2$O$_5$ in (010) projection [Nimmo et al., 1972].
Figure 2-13: Mechanisms whereby intergrowth phases may form at high temperatures. (a) coherent intergrowth of one row of Nb$_{25}$O$_{62}$ in H-Nb$_2$O$_5$; (b) coherent intergrowth of one row of Nb$_{12}$O$_{29}$ in Nb$_{25}$O$_{62}$; (c) regular coherent intergrowth corresponding to the phase Nb$_{53}$O$_{132}$ [Nimmo et al., 1972].
2.4 Laser-Heated Pedestal Growth (LHPG)

2.4.1 Introduction

2.4.1.1 Overview

Single crystal growth studies will serve two important purposes during the course of this material investigation. First, in order to determine the anisotropic bulk properties of the materials, it was essential to grow single crystals of required geometry and sizes. Second, the work carried out here validates the important technique for single crystal fiber growth (Laser Heated Pedestal Growth technique). The LHPG method is similar to the float zone technique. When the fiber diameter is smaller than the source rod diameter from which it grows, it is also known as pedestal growth. For heat sources, there are several types including resistance, induction, electron beam, focused lamp and laser heating which can be used to produce molten zones. Laser heating is a quite ideal heat source for the pedestal growth method because it can be tightly focused directly onto the sample with a beam size to produce the molten zone comparable with the fiber dimensions. It also can be used in ambient, inert, reactive or vacuum atmospheres.\textsuperscript{35}

This method has two main advantages: (i) there is no contamination from a crucible and (ii) the wide-range temperature control allowing the growth of crystal fiber of various high melting point materials. In addition, large temperature gradients are readily achievable permitting rapid growth. Typically, the growth rate, which is highly material dependent, several tens of mm/h or even mm/min and several orders higher than other techniques, is achievable. There is no intrinsic growth length limitation of single
crystal fibers. As long as the feed rods can be recharged continuously, the fiber length increases. Consequently, LHPG is suitable for the growth of crystals in one-dimensional configuration.

The investigations of the dielectric properties of many important systems in single crystal forms have been studied in the past two decades as this technique provide the desirable materials for measurements rather fast and in proper orientation.

2.4.1.2 Survey of Fiber Methodologies

There has been interest in crystalline materials prepared in fiber form for a sustained period of time; this is partially because single crystal fiber occurring naturally in the form of whiskers often possess near ideal physical properties in crystallinity and in tensile strength. Theses fibers were usually grown on solid surfaces by vapor phase reactions or in aqueous solutions, but they can also form spontaneously on plated metals or eutectic alloys. Earlier work addressed itself mostly to metallic materials, as early as 1922; Von Gomperz was successful in pulling single crystal metallic filaments directly from the melt. Later in the 1950’s, much of the work centered on the magnetic and mechanical properties of metallic whiskers, through vapor phase reactions or from aqueous solutions, did not allow the control of the fiber dimensions and often introducible variations in the whisker composition or characteristics. In 1958, Stepanov first suggested a method of growing large size, shaped crystals of various geometries and configurations; the method which now carries his name consists of forming a melt column in a definite shape through the use of metallic shaper and to crystallize the melt
after passage through the die. Stepanov and his co-workers were able to grow a great variety of materials in different shapes using a collection of shapers. This growth method using one particular die is shown in Fig. 2-14.a.

The fiber geometry is just another configuration that can be shaped and clearly the Stepanov method is adaptable to the growth of fibers. Indeed, other than the vapor and liquid phase growth methods mentioned earlier in connection with the growth of metallic whiskers, there are four other methods which have been utilized for the growth of crystalline fibers with controllable length and diameters.

a). Edge-defined film fed growth (EFG): In this method the fiber is grown from the melt contained in a capillary with well defined edges as shown in Fig. 2-14.b. The capillary is immersed in and is fed by a reservoir of molten material to be grown. This method was first employed by LaBelle and Mlavsky to grow long fibers of sapphire, lithium niobate and spinel. This is clearly a variant of the Stepanov method; however, LaBelle emphatically points out that whereas in the Stepanov method the melt column shape is used to control the shape of the crystal, EFG crystal shapes are controlled by the die and are independent of the melt column. In the latter, proper wetting of the capillary is essential for stable growth hence the choice of capillary materials is crucial; here, also, both the crucible holding the reservoir and the capillary themselves can be sources of contamination of the fiber.

b). Capillary-fed melt growth (CMG): this method of fiber synthesis is related to the Stepanov and the EFG methods. In CMG, however, the capillary is used as a conduit
to feed an appropriately shaped die that determines the shape and dimensions of the
fiber.\textsuperscript{42} The melt is either fed through gravitation or forced by pressurization through the
capillary into the shaper/crystallization regions\textsuperscript{43} (Fig.2-14.c) High optical quality single
crystal fibers of various heavy metal halides have been grown in this way; here again the
choice of materials for the capillary and for the die is determined by the same wetting and
contamination considerations as EFG.

c). \textit{Capillary-Bridgeman growth}: in this method, glass capillaries are immersed in
the melt of the crystal to be grown; the melt is then lowered through a temperature
gradient to crystallize the material inside the glass tube.\textsuperscript{44} Capillary-Bridgeman growth is
schematically illustrated in Fig.2-14.d. Because of the relatively low melting point of
glasses, this method is of usefulness principally in the growth of low melting point
materials such as organic crystals. Also limiting its general applicability is the necessity
of matching thermal expansion coefficients of the crystallizing solid and the glass
capillary and the requirement of chemical compatibility between the two media.

d). \textit{Float-zone or pedestal growth}: this is a miniaturized variant of the Czochralski
method of crystal growth.\textsuperscript{45} In this technique, the feed stock is generally in the shape of a
rod and a self supporting bubble of melt is formed at the tip of the rod. A number of
heating sources have been used to produce the melt; the most common method by far has
been laser heating with focused single or multiple beams. A seed id dipped into the melt
and is wetted by it; as the seed is pulled out, surface tension of the molten materials forms
a pedestal around the seed, hence pedestal growth. The seed/melt combination is pulled
out at a rate faster than the source rod is fed into the heating zone, resulting in a fiber of reduced diameter. The melt is kept in place solely by surface tension, hence, this fiber growth method does not require crucibles and eliminates one source of sample contamination. This type of containerless growth also permits the synthesis of materials with extremely high melting. The so-called Laser Heated Pedestal Growth (LHPG) method is illustrated in Fig 2-15.

No single approach can produce optical quality fibers of all materials. Since the emphasis of this thesis is on niobium-based oxide materials which have high melting point, the LHPG method offers the most versatility and convenience for their growth in fiber form.
Figure 2-14: Schematic representation of techniques to grow shaped crystals and fibers. (a) The Stepanov method. (b) The edged defined film fed growth (EFG) method. (c) The capillary fed growth (CFG) method and (d) The capillary Bridgeman growth method.
Figure 2-15: Schematic representation of the LHPG method for fiber growth showing the various regions involved in the growth.
2.4.2 The Laser-Heated Pedestal Growth Method

2.4.2.1 Background

The first application of laser radiation for the controlled melting of materials for crystal growth was carried out by Eickhoff and Gurs\textsuperscript{46} who used a high power CO\textsubscript{2} laser as the heating source in the floating zone growth of Ruby crystal back in 1969. In 1970, Gasson and Cockayne\textsuperscript{47} were able to melt various refractory oxides with melting temperatures in the 2000-2500°C range and were able to grow relatively large size crystalline rods at rates in the vicinity of 1-3 cm/h. Al\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, CaZrO\textsubscript{3}, and MgAl\textsubscript{2}O\textsubscript{4} were grown by this method successfully, whereas they were not able to obtain melts in the more volatile compound such as MgO and CaO. In 1975 Burris and Stone\textsuperscript{48} used a two beam, laser heated zone melting method known as Pedestal Growth\textsuperscript{49} to pull single crystal fiber of YAG:Nd of diameters in the tens of µm range and lengths of 0.1 to 1 cm. Takagi and Ishii (1977)\textsuperscript{50} applied this technique to the growth of LaB\textsubscript{6} and Al\textsubscript{2}O\textsubscript{3}. This initial work was accomplished using a two-beam configuration, where the initial laser beam was split into the hot zone 180° apart. This, however, resulted in a non-uniform heat distribution in the molten zone. In 1977, Haggerty et al.\textsuperscript{51} reported the adapted heating method by designing a patented four-beam laser heated float zone system specifically for the controlled growth of crystalline fibers. This development improves the energy distribution and solved the non-uniform heat distribution problem in the molten zone in two-beam configuration. Fibers were produced under a variety of growth conditions; that is by varying the atmosphere, as a function of pulling rates and pull
orientations and the dependence of laser power and stability parameters. Haggerty was able to grow fibers of sapphire and yttria as well as of some titanium compound (TiC, TiB₂). The two and four beam laser heating configurations of Haggerty and others could at time produce non-uniform heating and hence melting of the growth stock or undesirable thermal gradients in the molten zone depending upon the thermal properties and the dimensions of the feed rod. The majority of improvements were introduced by Feigelson⁵² and Byer⁴⁵ and their respective coworkers at Stanford in the early and mid 1980’s: these workers were able to design an optical system which produced a symmetrical, circular beam focus and a uniform molten region while providing a shadow or cooling region immediately above the melt. The optical system uses a so-called Reflaxicon and other focusing gold coated copper optics.

2.4.2.2 The LHPG method

LHPG and the related float zone growth techniques are micro-variants of the Czochralski growth method; the feed stock used is generally in the shape of a rod and the melt is in the form of a self supporting bubble at the tip of the rod. A number of heating sources have been used to produce the melt; the most common method by far has been laser heating with focused single or multiple beams. An appropriate seed is dipped into the melt and crystallization occurs at the seed/melt interface as the seed is pulled upwards out of the melt and away from further exposure the heating laser radiation. As the seed is pulled out, surface tension of the molten materials forms a pedestal around the seed, hence the name of pedestal growth. As material is fed into the crystallizing fiber, the
source rod is simultaneously fed into the heating zone in order to maintain a constant volume of melt. The diameter of the resulting fiber crystal is a function of the diameter of the source rod and the ratio of fiber pulling to source feeding speed. The melt is kept in place solely by surface tension, hence, this fiber growth method does not require crucibles and eliminates one source of sample contamination. This type of container-less growth also permits the synthesis of materials with extremely high melting points. The laser heated version of pedestal growth (LHPG) is illustrated in Fig. 2-15.

In a typical LHPG fiber pulling system, a stabilized CO\textsubscript{2} laser, typically with an output of between 50-180 W, is used as a heating source. The fiber pulling assembly may be enclosed in a vacuum-high chamber allowing growth in controlled atmospheres.

The preparation of source rods for fiber growth is very simple. Rods can be cut from single crystals or polycrystalline samples. To initiate the growth of a single crystal fiber, a Pt wire, tapered polycrystalline ceramic or single crystal can be used for seeding. The crystallographic orientation of the fiber is determined by the orientation of the seed. The source rods we have employed here at MRI are typically square cross section bars 1x1x50 mm\textsuperscript{3}. The pulling speeds are also typically 10-25 mm/hour. The detailed descriptions of the LHPG instrument facility at MRI and the growth procedure will be provided in Chapter 3.
2.4.2.3 Advantages of the LHPG Method of Fiber Growth

As experience was gained in the operation of LHPG apparatus, as the properties of the as grown fibers were characterized and these fibers were incorporated into actual optical devices, several advantages of this method of materials synthesis became apparent not only in the growth of fibers for applications but more importantly, as a general way to explore material synthesis and the properties of crystal growth.

As noted earlier, LHPG is a micro version of the Czocharalski and of the floating zone crystal growth techniques, hence, any material that can be grown in bulk by these two methods can in principle be pulled into fiber form. In addition, by proper focusing and by adjustment of laser power levels and source rod sizes, the LHPG method is capable of producing optical quality single crystal fibers of refractive materials with very high melting point; the ultimate temperature attainable is in practice limited only by the available power.

Other advantages of the LHPG method have also become apparent, as follows:

a) One of the most attractive features of the LHPG method is the rapidity with which fibers can be grown by this method; as we have noted already, pulling speeds of the order of 10-20 mm/h are usually employed or pulling faster as 1 mm/min. A fiber sample of length 1 or 2 cm is sufficient for spectroscopic characterization which also can be done quickly, if not in situ\textsuperscript{53} The information feed back made possibly by the combination of rate of growth and fast characterization of the desired fiber properties has allowed the rapid adjustment of stock compositions and growth conditions for optimized
materials. It is this feature of the LHPG method that makes it such a powerful tool in the synthesis and engineering of crystalline materials in general; with the rapid feed back, new and optimized crystals can now be prepared with turn around times of hours rather than days or weeks as is customary in other growth methods.

b) The LHPG relies solely on surface tension to maintain the integrity of the melt and hence it is a method of growth which does not require crucible; nor does the enclosure containing the fiber growth region possess walls heated to high temperatures as is the case in crystal growth furnaces. Both crucible and furnace surfaces are generally understood to be the primary source of unintentional contamination in crystal growth, hence, it follows that the absence of these surfaces allows the growth of very pure crystal fibers. Purities in LHPG fibers are solely determined by the purity of the starting materials used in the formation of the source rods.

c) The source rods as well as the melt volume in LHPG are typically small and are on the order of 10 and 1 mm³, respectively. The cost of the chemical compounds required for the growth of single crystal fibers is, as a consequence, relatively small and very much within reason. Because of this, it is possible to grow fiber crystals of materials which would be prohibitively expensive to grow in bulk, especially on trial basis. Further, it is also generally accepted that thermal gradients within the melt container are responsible for introducing stresses and other defects in bulk crystals; as again no container is required to contain the small melt volume, LHPG pulled fibers can be made
practically stress free. Annealing and retreatment of the fibers also reduces other defects so that these fibers can be made to possess very good crystalline and tensile properties.\textsuperscript{54}

d) The possibility of fiber growth from either congruent or incongruent melt materials\textsuperscript{55,56}

e) Finally, for some of us interested in the optical spectroscopic properties of activated materials, the fiber configuration is ideal experimentally for conducting absorption, emission and ancillary dynamical and static optical measurements.\textsuperscript{57}
2.5 References


This chapter describes the processing techniques which were employed to prepare the ceramic and single crystal specimens. The general details of each process are presented here including the material characterizations.

### 3.1 Ceramic Processing

#### 3.1.1 Material Systems

This research was emphasized on the niobium-based oxide materials. Niobium pentoxide (Nb₂O₅) was doped by the small substituents of simple oxides including TiO₂, SiO₂, and Al₂O₃ in the amount of 5%, 8%, and 11% by mole as given below:

\[
\begin{align*}
\text{Nb}_2\text{O}_5(0.95) & : \text{TiO}_2(0.05) & \quad \text{Nb}_2\text{O}_5(0.95) & : \text{SiO}_2(0.05) & \quad \text{Nb}_2\text{O}_5(0.95) & : \text{Al}_2\text{O}_3(0.05) \\
[\text{N95T5}] & \quad [\text{N95S5}] & \quad [\text{N95Al5}] \\
\text{Nb}_2\text{O}_5(0.92) & : \text{TiO}_2(0.08) & \quad \text{Nb}_2\text{O}_5(0.92) & : \text{SiO}_2(0.08) & \quad \text{Nb}_2\text{O}_5(0.92) & : \text{Al}_2\text{O}_3(0.08) \\
[\text{N92T8}] & \quad [\text{N92S8}] & \quad [\text{N92Al8}] \\
\text{Nb}_2\text{O}_5(0.89) & : \text{TiO}_2(0.11) & \quad \text{Nb}_2\text{O}_5(0.89) & : \text{SiO}_2(0.11) & \quad \text{Nb}_2\text{O}_5(0.89) & : \text{Al}_2\text{O}_3(0.11) \\
[\text{N89T11}] & \quad [\text{N89S11}] & \quad [\text{N89Al11}] 
\end{align*}
\]

Their solid-solutions were prepared by the conventional mixed oxide method, discussed in the next section. The starting chemicals with purity specification are listed in Table 3-1.
Table 3-1: Starting chemicals used in this investigation

<table>
<thead>
<tr>
<th>Materials</th>
<th>Melting Point</th>
<th>Purity</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niobium (V) oxide Nb₂O₅</td>
<td>1520°C</td>
<td>99.9985%</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>Titanium (IV) oxide TiO₂</td>
<td>1830°C</td>
<td>99.99%</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>Silicon (IV) oxide SiO₂</td>
<td>1710°C</td>
<td>99.999%</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>Aluminium oxide Al₂O₃</td>
<td>2045°C</td>
<td>99.995%</td>
<td>Johnson Matthey</td>
</tr>
</tbody>
</table>
3.1.2 Solid-State Reaction

The samples prepared in this study were primarily ceramics, prepared using the conventional solid state mixed oxide method. High purity oxides were weighted out in their respective proportions and added to a polyethylene bottle. The powder mixtures were wet ball-milled in a polyethylene bottle for 24 hours using alcohol as dispersion agent and zirconia (ZrO₂) balls as grinding media. The zirconia balls are in such a quantity that the rotation of the mill causes it to cascade, so that both a shearing and a crushing action is applied to any material lying between the milling elements. For efficient action the real volume of the material to be milled should be about a third of that of the milling media (zirconia balls). The volume of liquid must be sufficient to form a freely flowing cream, usually between 100% and 200% of the volume of the powder. Drying followed ball mixing and the mixture was completely dried in the oven at 80°C for 24 hours. This ensures complete removal of volatile material from the powder. After drying, the powder was reground with a mortar and was sieved using a Standard Testing Sieve (A.S.T.M.E.-11 specification) with a Tyler equivalent of number 140 mesh sieve.

The next step is calcination. Calcination causes the constituents to interact by interdiffusion of their ions and so reduces the extent of the diffusion that must occur during sintering in order to obtain a homogeneous body. Calcination conditions are important factors controlling shrinkage during sintering. Calcining conditions were first optimized through differential thermal analysis (DTA) to determine the minimum calcining temperature to achieve the desired single phase. Powder x-ray diffraction was used to check whether the desired single phase was obtained.
Following calcinations, the calcined powder was ball milled again for 24 hours using zirconia balls and ethyl alcohol as the medium. The second ball milling was aimed to reducing the particle size of the calcined powder. The ball milled powder was dried at 80°C again and then was sieved through 140 mesh. Then, the sieved powder was prepared for the pellet formation. Acryloid binder was added at 3-4 wt% to the powder and acetone was used to produce a viscous thick paste. The mixture was continuously agitated until the acetone and other volatile components had evaporated, leaving the fine powder, free of large aggregates.

One of the most important requirements for a binder is that it should be possible to eliminate it from the compact without any disruptive effect. When particles are in high concentrations in a fluid they tend to form a continuous network with points of direct, or almost direct, contact between them. These points of contact remain when the binder is volatilized or burned out and provide, through Van der Waals force, sufficient strength to resist the disintegrating effect of small stresses.

It is important that the binder be distributed throughout the bulk of the powder. A thin layer of the binder should coat each particle of the calcined powder. The procedure followed to achieve this was to dissolve the appropriate quantity of the binder in acetone. After the binder completely dissolved in acetone, the powder was added to this solution and stirred well until the acetone evaporated and left the powder dry. This process was repeated one more time, to ensure that the binder coated the particles evenly. The powder was ground and sieved through the mesh. The powder is now ready to be pressed for pellet formation.
The circular pellets were pressed uniaxially using a steel die and hydraulic press. A hydraulic laboratory press (Carver, Inc.) was used to press ½ inch diameter pellets with an applied load of approximately 10000 lbs. The hardened steel die was lubricated using a very light coating of spray-on cooking oil (PAM, International Home Foods Inc.). The pellets were typically 10 mm in diameter and 1 mm in thickness for dielectric measurement and other measurements, and 1 3/8 inch in diameter and 5 mm in thickness for preforms in LHPG. The green pellet was then placed in a flat alumina crucible and transferred to a furnace for binder burnout. The binder burnout profile is shown in Fig 3-1. After burnout, the pellet was placed on a flat platinum foil and sealed in the crucible, ready for sintering.

Various sintering conditions were tried out on each sample composition, to arrive at the optimum sintering conditions. In all cases sintering was carried out in an oxidizing atmosphere of air so that the constituent elements could retain their highest oxidation states. The sintered pellet was polished using alumina powders of various particle sizes in order to obtain smooth surfaces that are parallel to each other. Again, the X-ray diffraction pattern was obtained to verify the phase and crystallographic data. This has been the overall procedure followed in this investigation to prepare high quality ceramic samples of the materials under investigation. The flow diagram for sample preparation described above is shown in Fig. 3-2. However specific conditions for sample preparation might vary a little bit depending on the material we deal with. Table 3-3 deals with the specific conditions under which the samples for each individual materials were prepared.
Figure 3-1: Typical binder burnout profile.
Mix stoichiometric quantities of oxides

Wet milling & Drying

Grinding & Sieving

Calcination

Single phase analysis by powder X-ray diffraction

Yes

Wet milling & Drying

Add 3-4 wt% binder
Grinding & Sieving

Uniaxially pressing pellet

Binder burnout & Sintering

Polishing

No

Figure 3-2: Flow diagram of ceramic preparation by conventional oxide mixing method.
3.1.3 Ceramic Characterization

3.1.3.1 X-ray diffraction characterization (XRD)

To analyze the phase formation and the effect of solubility on the phase stability, X-ray diffractometry (XRD) was conducted on each of the samples mentioned above using Cu Kα radiation (Scintag PAD V, Scintag Inc., Cupertino, CA). The power settings used for the generator were 45 kV and 40 mA. The sintered pellets were crushed to avoid the preferential crystallographic orientation, and the crushed powder was placed in a zero background silica holder. X-ray diffraction data were collected between 10° and 70° 2θ at a rate of 2° 2θ/min, unless otherwise specified.

3.1.3.2 Density measurement

Density was measured using the standard xylene measurement technique. In this technique, the weight of the sample in air was measured, following which it was completely immersed in xylene and the weight was again noted. Then the sample was removed, its surface swiftly wiped off any excess xylene and the weight of the damp sample was measured. Using these three measurements, the density of the sample can be calculated by the simple formula given below:

$$Density = \left( \frac{A}{B - C} \right) \times D_{\text{xylene}}$$

(3.1)

Where 

A = weight of the sample in air

B = weight of the sample immersed in xylene
C = weight of the damp sample after being wiped off excess xylene

\[ D_{\text{xylene}} = \text{density of xylene (0.861075 gm/cc)} \]

The density of the sintered sample was calculated in this fashion. The xylene technique is fast, simple and reliable to quickly determine the density of a sample. The method is based on the principles of buoyancy. Also in the case of low density samples, where there are more open pores, it is preferable to use a liquid that has a low surface tension. Xylene satisfies this criterion and is also a reasonably viscous liquid.

### 3.1.3.3 Scanning Electron Microscopy (SEM)

Microstructure features of the ceramics and single crystals were examined using an S-3500N scanning electron microscope (Hitachi Ltd., Tokyo, Japan). SEM analysis provided both sintered surface and fracture surface including grain size and shape. The surface of each sample can be prepared in different ways ranging from the fresh sintered surface or fractured surface to the polished surface and thermally etched surface. The thermal etching was carried out at 200°C below sintering temperature for 5 min. All samples were sputter-coated with a thin Au film prior to SEM observation to increase electrical conductivity at the surface and prevent charging that tends to decrease image clarity. The energy dispersion spectrum (EDS) which is attached to SEM instrument was employed to analyze the distribution of elements.
3.1.4 Ceramics of Nb₂O₅(1-x):TiO₂(x)

The starting chemicals in the present study were 99.9985% pure Nb₂O₅ and 99.99% TiO₂, supplied by Johnson Matthey Company as Puratronic grade inorganic chemicals. The investigated compositions contained Nb₂O₅: TiO₂ = 1-x : x with x=0.05, 0.08, and 0.11 mole%. High purity niobium and titanium oxides were weighted out in their respective proportions, and then were followed the solid-state reaction as described in section 3.1.2. The calcining conditions were first optimized through differential thermal analysis (DTA) to determine the minimum calcining temperature to achieve the desired single phase. DTA scan were run on a Perkin-Elmer thermal analysis system from room temperature to 1400°C at a rate of 10°C/min, and is presented in Fig. 3-3.

Data on the phase relationships in the niobium (V) oxide-titanium (IV) oxide are contradictory.1-3 The most recent phase diagram⁴ was constructed to define the phase formation in the Nb₂O₅-TiO₂ system more precisely as shown in Fig. 3-4. This diagram was useful to the determination of calcining and sintering temperature of Nb₂O₅(1-x):TiO₂(x). From this diagram, if we need 5-11 mole% TiO₂ dissolved in Nb₂O₅ and yields the pure phase (monoclinic of β-Nb₂O₅ solid-solution); the heating reaction should be reached 1300°C. Many researchers⁵-¹⁰ had reported that all varieties of Nb₂O₅ polymorphs rapidly transformed to a high temperature stable form of monoclinic H-Nb₂O₅ at 1100°C. This diagram also suggested the melting temperature of these solid-solutions at nearly 1500°C, subsequently the sintering temperature should be set at 100°C-200°C lower than the melting point.
Figure 3-3: DTA pattern of mixed-oxide powder Nb₂O₅(0.92):TiO₂(0.08).
Figure 3-4: Equilibrium diagram of the Nb₂O₅-TiO₂ system: M = solid solution based on β-Nb₂O₅ (monoclinic), A = 2TiO₂.5Nb₂O₅ (orthorhombic), B = TiO₂Nb₂O₅ (monoclinic), Tr = solid solution based on TiO₂ (tetragonal, rutile type). [After Babich et al. (1988)]
Based on the information provided above, the pellets of each composition were calcined at 1300°C for 24 hours and sintered at 1400°C for 24 hours. The well reacted pellets with density approximately 94% of theoretical density were obtained by the above condition.

3.1.4.1 Microstructure observation by Scanning Electron Microscopy

The Nb$_2$O$_5$(0.92):TiO$_2$(0.08) sintered pellet was chosen to observe the microstructure by SEM technique. Figure 3-5 shows the scanning electron micrograph of the fracture side. It presents the non-equiaxed grain shapes. If the grain shape was altered by processing so that the grains are no longer equiaxed in shape, this fact can suggest the sintering temperature and time seem too high. Sintered surface of the pellet was polished (using SiC powder 14 µm, 12.5 µm → Al$_2$O$_3$ powder 3 µm, 1 µm → diamond paste 1 µm, 0.25 µm) and thermally etched to observe the grain size and grain boundary. The micrograph of thermal etching sample, Fig. 3-6, shows the improvement of quality image that could not be seen from Fig. 3-5. It reveals the grain boundaries so the grain shape and the grain size can be determined. The thermal treatment (etching) is apparently effective in revealing boundaries because there is a large driving force for surface diffusion. The non-equiaxed grain shapes are visible and clear. Since the calcined ground powder was ground for a long period of time, the large and elongated grains may occur during the processing. The growth feature lines which show explicitly on the grains suggest the presence of grain growth during the processing.
Figure 3-5: SEM micrograph of Nb$_2$O$_5$(0.92):TiO$_2$(0.08), fracture surface, 1000x.
Figure 3-6: SEM micrograph of Nb$_2$O$_5$(0.92):TiO$_2$(0.08), thermal etching surface, 4000x.
3.1.4.2 Phase identification by X-ray diffraction

To conduct the baseline check on crystallographic phases of the sintered pellets, powder x-ray diffraction patterns were recorded using a Scintag diffractometer. The room temperature XRD patterns of Nb$_2$O$_5$(1-x):TiO$_2$(x) ceramics are shown in Fig. 3-7. The XRD patterns of these solid-solutions are not available in JCPD database. Therefore, pure phase Nb$_2$O$_5$ pattern was used with tolerance of minor peak shift. Nb$_2$O$_5$ is oxide of complicated stoichiometry and, in particular, can exist in one crystalline phase within a wide O/Nb range. Thus, the XRD of Nb$_2$O$_5$ and its polymorphs are complex. Reference PDF card of Nb$_2$O$_5$ was carefully chosen to fit the patterns of ceramics.

The XRD patterns of all compositions in Fig.3-7 were similar in their complexity and the phases present. However, the existence of Magneli phases (Nb$_{2-\delta}$O$_5$) i.e. Nb$_{12}$O$_{29}$, Nb$_{22}$O$_{54}$, Nb$_{47}$O$_{116}$, Nb$_{25}$O$_{62}$, and Nb$_{52}$O$_{132}$ is possible so it is needed to be carefully observed. The use of Cu K$_\alpha$ radiation for phase identification of the Magneli phases was relatively easy when the XRD peaks within 20 = 17° to 20° were studied; however, other than that it was difficult.

The XRD patterns of all compositions yield the best matching to monoclinic crystallographic system which is the high temperature form of H-Nb$_2$O$_5$. No separation of phases of TiO$_2$ were found. Each composition was indexed to a monoclinic cell with lattice parameter a, b, c, and angle $\beta$. Table 3-2 is a summary of the lattice parameters using the least square refinement. The structure refinement was carried out using the data obtained from XRD using proprietary refinement program. The program determines the best-fit of the (hkl) phases corresponding to the d values provided by the XRD data.
Table 3-2: Summary of lattice parameters of Nb$_2$O$_5$(1-x):TiO$_2$(x) ceramics

<table>
<thead>
<tr>
<th>Ceramics</th>
<th>Monoclinic lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
</tr>
<tr>
<td>Nb$_2$O$_5$*</td>
<td>20.381</td>
</tr>
<tr>
<td>N95T5</td>
<td>20.375</td>
</tr>
<tr>
<td>N92T8</td>
<td>20.360</td>
</tr>
<tr>
<td>N89T11</td>
<td>20.358</td>
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</tbody>
</table>

* PDF card # 37-1468
Figure 3-7: XRD patterns of Nb$_2$O$_5$(1-x): TiO$_2$(x), x=0.05, 0.08, 0.11, ceramics.
3.1.5 Ceramics of Nb$_2$O$_5$(1-x):SiO$_2$(x)

The starting chemicals were 99.9985% pure Nb$_2$O$_5$ and 99.999% SiO$_2$, supplied by Johnson Matthey Company as Puratronic grade inorganic chemicals. The investigated compositions contained Nb$_2$O$_5$: SiO$_2$ = 1-x : x with x=0.05, 0.08, and 0.11 mole%. High purity niobium and silicon oxides were weighed out in their respective proportions, and then were processed by the solid-state reaction as described in section 3.1.2. The calcining conditions were first optimized through differential thermal analysis (DTA) to determine the minimum calcining temperature to achieve the desired single phase. As seen from Fig. 3-8, the DTA pattern of the mixed-oxide powder of Nb$_2$O$_5$(0.92):SiO$_2$(0.08), the mixed-oxide powder starts to react with each other at temperature higher than 1200°C and then melts at temperature of 1491°C. The calcined temperatures were tried out from 1250°C to 1350°C. The calcining temperature of 1300°C yields the best XRD pattern, matching to the single phases of monoclinic structure. The sintering temperature should be lower than the melting point of the solid solution and should not be too high to allow the occurrence of Nb$_2$O$_5$ liquid phase.

Figure 3-9 shows the SEM micrograph of ceramic microstructures sintered at different temperatures. At 1300°C, the distributions of grain shapes and grain sizes were presented including much of porosity. The elongated grains with preferred orientation were observed in the ceramic sintered at 1400°C which is the selective temperature for sintering Nb$_2$O$_5$(1-x):SiO$_2$(x) ceramics. The XRD patterns of these ceramics are illustrated in Fig. 3-10, yielding the results of monoclinic single phase.
Figure 3-8: DTA pattern of mixed-oxide powder Nb₂O₅(0.92):SiO₂(0.08).
Figure 3-9: SEM micrographs of Nb$_2$O$_5$(0.92):SiO$_2$(0.08) ceramics, sintering at different temperatures.
Figure 3-10: XRD patterns of Nb$_2$O$_5$(1-x):SiO$_2$(x), x=0.05,0.08,0.11, ceramics.
3.1.6 Ceramics of Nb₂O₅(1-x):Al₂O₃(x)

The starting chemicals were 99.9985% pure Nb₂O₅ and 99.99% Al₂O₃, supplied by Johnson Matthey Company as Puratronic grade inorganic chemicals. The investigated compositions contained Nb₂O₅: Al₂O₃ = 1-x : x with x=0.05, 0.08, and 0.11 mole%. High purity niobium and aluminum oxides were weighed out in their respective proportions, and then were processed by the solid-state reaction as described in section 3.1.2. The same strategies as described above were used to obtain the proper calcining and sintering temperatures for Nb₂O₅(1-x):Al₂O₃(x) ceramic processing. The calcining temperature of 1350°C for 3 hours and sintering temperature of 1450°C for 3 hours were employed. It is generally known that Al₂O₃ is a refractory material with high melting point (~2045°C) and hence the processing temperatures are higher than those of Nb₂O₅(1-x):TiO₂(x) and Nb₂O₅(1-x):SiO₂(x) ceramics.

Theoretical density of about ~ 94% was obtained for ceramics, see Table 3-3. The microstructure of Nb₂O₅(0.92):Al₂O₃(0.08) was taken by SEM, as seen from Fig. 3-11. X-ray diffraction peaks revealed the same kind of crystal structure as Nb₂O₅(1-x):TiO₂(x) and Nb₂O₅(1-x):SiO₂(x) ceramics.
Figure 3-11: SEM micrograph of Nb$_2$O$_5$(0.92):Al$_2$O$_3$(0.08) ceramic.
Figure 3-12: XRD patterns of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x), x=0.05, 0.08, 0.11, ceramics.
Table 3-3: Summary of ceramic processing conditions

<table>
<thead>
<tr>
<th>Materials</th>
<th>Powder mixtures</th>
<th>Calcining Condition</th>
<th>Sintering Condition</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>N95T5</td>
<td></td>
<td>1300°C/24 h</td>
<td>1400°C/24 h</td>
<td>93.4%</td>
</tr>
<tr>
<td>N92T8</td>
<td>Nb$_2$O$_5$, TiO$_2$</td>
<td>1300°C/24 h</td>
<td>1400°C/24 h</td>
<td>93.6%</td>
</tr>
<tr>
<td>N89T11</td>
<td></td>
<td>1300°C/24 h</td>
<td>1400°C/24 h</td>
<td>93.8%</td>
</tr>
<tr>
<td>N95Si5</td>
<td></td>
<td>1300°C/24h</td>
<td>1400°C/3h</td>
<td>95.3%</td>
</tr>
<tr>
<td>N92Si8</td>
<td>Nb$_2$O$_5$, SiO$_2$</td>
<td>1300°C/24h</td>
<td>1400°C/3h</td>
<td>94.9%</td>
</tr>
<tr>
<td>N89Si11</td>
<td></td>
<td>1300°C/24h</td>
<td>1400°C/3h</td>
<td>94.5%</td>
</tr>
<tr>
<td>N95Al5</td>
<td></td>
<td>1350°C/24h</td>
<td>1450°C/3h</td>
<td>94.8%</td>
</tr>
<tr>
<td>N92Al8</td>
<td>Nb$_2$O$_5$, Al$_2$O$_3$</td>
<td>1350°C/24h</td>
<td>1450°C/3h</td>
<td>94.5%</td>
</tr>
<tr>
<td>N89Al11</td>
<td></td>
<td>1350°C/24h</td>
<td>1450°C/3h</td>
<td>94.1%</td>
</tr>
</tbody>
</table>
3.2 Single Crystal Growth by the Laser-Heated Pedestal Growth Technique

3.2.1 Laser-Heated Pedestal Growth Equipment

The Laser-Heated Pedestal Growth (LHPG) station used in MRI consists of a power source (laser generation system) with an optical layout, a growth section (growth chamber), and an observation and measurement system. The schematic drawing of the LHPG equipment is shown in Fig. 3-13. The whole station was placed on a customer designed Newport high performance optical table top to stabilize the whole system. The photograph of the whole LHPG station is shown in Fig. 3-14.
Figure 3-13: Schematic drawing of the Laser-Heated Pedestal Growth (LHPG) equipment.
Figure 3-14: Photographic picture of the whole LHPG station.
3.2.1.1 Power Source (Laser generation system)

The infrared radiation was produced by an Edinburgh Model PL6 step-tunable CW CO2 laser which was designed to give high output power with good frequency and stable amplitude. On the strongest line, the output power could reach 180 W\(^{14}\). During this study, the wavelength of the laser was fixed at 10.59 \(\mu\)m, and TE\(_{00}\) mode was used. The laser was controlled by both the power supply (Model LPS-2000) and gas handling system (Model 216). The output power level was first selected by the tube pressure, where higher pressure resulted in higher power output. The finer control of the output was realized by adjusting the power supply current. The long term frequency stability was achieved by a piezoelectric laser frequency stabilizer (Model 209).

The laser beam was introduced into the growth chamber by using eight 45\(^\circ\) reflection-coated mirrors after it excited the laser tube. A lasnix IR attenuator (Stuttgart, Germany) was on the optical route to allow the accurate step attenuation of the output laser power and to increase the growth temperature stability by allowing the laser tube working at normal discharge current level.

3.2.1.2 Growth Section (Growth chamber)

Passing through a zinc selenide window in the growth chamber, the laser beam was incident upon the apex of the inner mirror cone of the reflaxicon, which consisted of a primary conical mirror surrounded by a larger conical mirror. Both conical mirrors were coaxially located parallel with respect to each other and had identical conical angles of
45°. This set-up of reflaxicon converted a solid circular beam into an annulus ring with minimum radiation loss.\textsuperscript{15}

Once the beam left the reflaxicon, it was reflected off a doughnut shaped mirror located 45° to the beam traveling direction with the center hole allowing the vertical translation of the upper pulling head. This 45° mirror directed the radiation annulus down onto a parabolic mirror, which focused the radiation back to the focal point, forming the hot zone. When properly aligned, the hot zone was characterized by a circular uniform energy distribution. This parabolic mirror also has a hole in the center to pass the lower feeding head. An optical layout inside the growth chamber is illustrated in Fig. 3-15.

The growth chamber was an ultra-high vacuum chamber with \( \frac{3}{4} \) inch thick stainless steel walls (Hayward, CA). The chamber served to eliminate the air current disturbance and allowed crystal growth in other atmosphere conditions than air.

The translation of the feed and the seed rod was controlled by the high precision stepper motors manufactured by Crystalox, Ltd (Wantage, UK). The stepper motors (Model DPH4000) are five-phase microsteppers with 10,000 steps per revolution. A single step increment produced a 0.25 \( \mu \)m translation in the pullshaft. They are capable of translational motion from 0.001 mm/hr to 999.9 mm/min with an accuracy of 0.1%. With two additional stepper motors, rotational rates of 0.0001 to 99.99 rpm were possible with an accuracy of 0.1%. Two 300 mm long solid stainless steel pullshaft connected the stepper motors to two goniometers inside the growth chamber. An anti-vibration flexible coupler was used to connect the pullshafts and stepper motors to minimize vibration.
Figure 3-15: Schematic drawing of LHPG growth chamber and inside optical layout.
3.2.1.3 Observation and Measurement System

The growth process was observed from the symmetrical observation window located on both front and back sides of the growth chamber. A Questar QM1 telescope (New Hope, PA), located in the back of the growth chamber was an extremely short focal length telescope with a resolution of 3 µm at 22 inches. The telescope transferred the image to a Sony CCD video camera (Model XC-77) and an image was then viewed on a 12 inch Sony PVM-122 video monitor. Polarizing filters were placed in front of the CCD camera to reduce glaze of the image caused by high temperature in the hot zone.

The hot zone temperature was monitored by the PYRO micro-optical pyrometer manufactured by Pyrometer Instrument CO., Inc. (Northvale, NJ). It was placed in front of the front observation window of the growth chamber and it is capable of precision high temperature measurements on small targets to 0.0005 inch. The measurable temperature range is 700 to 3200°C with the repeatable precision intensity matching capability to 2-3°C. Temperature of the hot zone can be controlled by the output laser power.

The measurement of the output laser power was achieved by Apollo laser power meter (Model 101) with resolution of 0.1 Watts. The detector was placed right behind the IR attenuator on the optical route when needed.

3.2.2 Feed/Seed Preparation

The preforms or starting feed/seed rods were all prepared in the same manner using the mixed oxide method as described in ceramic processing section. The calcined
powder was pressed to form a pellet in a 1 3/8 inch diameter circular die, using approximately 20,000 psi pressure. The green pellets were typically 5 mm thick. The pellet was then placed in the furnace for binder burn out and sintering. Sintering conditions were varied depending on the type of materials.

The sintered pellet was sliced into wafers approximately 2 mm thick using a Buehler Isomet diamond saw. The surface of the wafer was sanded flat using silicon carbide polishing powder with various particle sizes. Usually, the wafer was polished to thin down to the thickness of 1 mm, corresponding to the preform dimensions.

The thin wafers were cut in square rods using a Precision Motors diamond-edged wafer saw. The rods were then repositioned to cut a square end, removing the outer pellet surface from the rod. This end was used as the growth end of the preform. The preforms were thoroughly soaked in acetone to remove cutting oils and other organic contaminants and air dried. The final feed-rod dimension used in this investigation was 25 x 1 x 1 mm$^3$. The seed-rod was also cut from the ceramic preform as no single crystal seed was available for these materials. The dimension of seed-rod was 5 x 1 x 1 mm$^3$.

### 3.2.3 Laser Preparation and System Alignment

After the tube pressure was set and the laser had stabilized, the power meter was put in line and the power was maximized, by the adjustment of the back grating. Since the laser output was radiated at the wavelength which was invisible to the human eyes, the spot size and shape of the laser output mode was visualized by a Luminescent sensor plate in the beam path by placing in front of the ZnSe window of the growth chamber.
The circular symmetric laser mode was realized by carefully adjusting the output grating. The piezoelectric frequency stabilizer was used to keep the laser mode stable during the growth process.

Once a stable circular beam spot was obtained, the position of the beam relative to the reflaxicon was adjusted. The beam position was checked by the burn shape on the facsimile paper put in front of the reflaxicon. The adjustment of the beam position was accomplished by changing the horizontal and vertical positions of the two 45° mirrors on the optical table.

Using the magnified images on CCD video camera, the He-Ne laser was then used to roughly position the feed-rod at the focal point of the parabolic mirror and, once accomplished, the low power CO₂ beam was let into the growth chamber to finely adjust the feed-rod position. The feed-rod position was adjusted by the translation stages on the goniometer. Alignment was a trial and error procedure because the adjustment knobs of the goniometer stages cannot be accessed while the feed-rod was in the hot zone. After the adjustment, the laser beam was blocked. The seed-rod was then positioned on top of the feed-rod. The feed-rod was positioned first because in the fine adjustment with the CO₂ laser, the tip of the feed-rod melted and a small round bulb was formed, which was undesirable for seeded growth.

The laser power required to form a molten zone was dependent upon several parameters: melting temperature, feed-rod diameter, thermal conductivity, effective emissive of the material of interest. Typically 10-15 watts of power was sufficient to melt an oxide feed-rod of 500 µm in diameter.
3.2.4 Growth Procedure

After the adjustments were made as described above the system was ready to begin growth. The feed and seed-rod were brought back into the hot zone position with a small gap to allow the volume change from the solid phase to liquid phase. The laser beam was introduced back to the growth chamber with low power first to start the melt of the tip of feed-rod. Then the seed-rod was moved down to touch the tip of melted feed-rod while the laser beam was increased the power. Once the seed had touched the molten tip, the translation direction was reversed, and the laser power was adjusted to achieve the desired zone shape. The stepper motors were set to the desired pulling and feeding rates and crystal growth was initiated. The stable molten zone shapes of each material will be discussed in the next section. Figure 3-16 shows the growth process as described above. The whole growth process was performed in an air atmosphere with no seed or feed rotation. The pulling ratio of seed/feed-rod is depended on types of materials.
Figure 3-16: Schematic drawing of the growth process: (a) the feed-rod was moved up to the hot zone, (b) the formation of molten tip, (c) the seed-rod was moved down to touch the molten tip, (d) the pulling of single crystal.
3.3 Single Crystal Growth of Nb$_2$O$_5$

3.3.1 Molten Zone Stability and Shape

The successful growth of single crystals using the float zone technique depends upon the stability of the molten zone, and the zone stability has been theoretically and experimentally studied by many investigators. Several parameters had been addressed including gravitational forces, small crystal diameters, zero gravity, and the meniscus angle of the molten zone.$^{17-19}$

The meniscus angle of the molten zone is a major factor in maintaining the shape of the growing crystal.$^{20}$ The meniscus angle is the angle between the tangent of the melt-gas interface at the tri-junction and the growth axis (Fig. 3-17). A necessary condition for growing a uniform cross-section of the resultant crystal is that the meniscus angle $\Phi$ should be maintained at a constant value $\Phi_0$. For a given growth system, the value of $\Phi_0$ is a property of the material and it is often independent of the growth rate, zone length and doping.$^{22}$

Recently, H-J. Lim et al. (2000)$^{23}$ had suggested that perhaps the most important factor influencing molten zone stability in the LHPG method, and therefore diameter uniformity and compositional homogeneity, is the variation of laser beam power with time. The beam power of our laser varied between 10 and 15%. Even small power excursions can change the molten zone temperature and thereby, its size. These fluctuations in zone length and perhaps shape can affect both the diameter of the crystal and its growth stability.
Figure 3-17: Schematic drawing of the solid-liquid-vapor tri-junction point and the meniscus angle; a) meniscus angle $\Phi_0 < 0$, b) meniscus angle $\Phi_0 > 0$. 
3.3.1.1 Nb$_2$O$_5$

The Nb$_2$O$_5$ single crystals were grown by using randomly selected seed rods such as <100> SrTiO$_3$ single crystal, <110> SrTiO$_3$ single crystal, and Nb$_2$O$_5$ ceramic. By using single crystals with known orientation as seeds, the molten zone could not form because the seed and feed rods did not touch each other. That means the <100> and <110> are not the preferred orientation of the growth axis. By using its own composition ceramic as a seed, the Nb$_2$O$_5$ single crystal was successfully grown. The molten zone was stable in the temperature range of 1500-1536°C with the shape of negative meniscus angle, as seen in Fig. 3-18.

3.3.1.2 Nb$_2$O$_5$-TiO$_2$

Molten zones were typically unstable during all Nb$_2$O$_5$(1-x):TiO$_2$(x) growth and pulsated along the growth direction. This instability may be related to (1) laser power, and therefore, temperature fluctuations, (2) the incongruent melting behavior of these solid-solutions, and/or (3) phase instability due to variations in or incorrect oxygen reduction. The micro-bubbles were observed inside the molten zone during growth which could possibly be originated from the porous ceramic.

Molten zone of Nb$_2$O$_5$(1-x):TiO$_2$(x) growth was a negative meniscus angle shape. The negative angle tended to increase during growth and the surface tension was collapsed at a critical meniscus angle. Growing fibers with a negative angle made it very difficult to control fiber diameter for a long period of time. However, with a proper reduction ratio and molten zone temperature, the molten zone could be maintained until
the growth was accomplished. The fluctuated molten zone yielded the non uniform
diameters of single crystal. The temperatures of molten zone were varied depending on
the amount of TiO$_2$ dopant as summarized in Table 3-5. The photograph of molten zone
detected from TV monitor is illustrated in Fig. 3-18.

### 3.3.1.3 Nb$_2$O$_5$–SiO$_2$

The growth of Nb$_2$O$_5$(1-x):SiO$_2$(x) single crystals was easier to control than the
growth of Nb$_2$O$_5$(1-x):TiO$_2$(x) solid solutions. The shape of molten zone was stable with
positive meniscus angle. No micro-bubbles formation inside molten zone was observed.

### 3.3.1.4 Nb$_2$O$_5$–Al$_2$O$_3$

The molten zones of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) single crystal were stable throughout
the growth. The molten zone shape has a negative meniscus angle which was constant
during the whole growth process. The volume of molten zone was larger than those of
other Nb2O5 based oxide growths because the higher laser power was used to melt the
Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) ceramic. Figure 3-18 shows the molten zone photographs of all
single crystals previously described.
Figure 3-18: Photographs of molten zones which were formed during the growth of Nb$_2$O$_5$, Nb$_2$O$_5$(1-x):TiO$_2$(x), Nb$_2$O$_5$(1-x):SiO$_2$(x), and Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) single crystals.
3.3.2 Growth Rate

The effect of growth rate on the crystal quality of single crystal fibers was first studied on alumina, where very rapid speeds resulted in the formation of microvoids.\textsuperscript{24}

Microvoid formation was attributed to dendritic growth caused by supercooling at the freezing interface. It has also been proposed that the density difference between the liquid and solid is the origin of the microvoids.\textsuperscript{25} Nightingale\textsuperscript{26} found the shape of the freezing interface also changed from concave to convex at high growth speeds.

The reduction ratio is one important parameter for the constant crystal diameter. The reduction ratio is the ratio between the pulling rate to the feeding rate. Under steady-state conditions, there is balance of the mass entering and leaving the molten zone, therefore, a constant reduction ratio results in approximately equal crystal diameters for each run. The constant crystal diameter eliminated the contributions of radial temperature gradients to the results.

The effect of growth rates on an incongruently melting compound has not been investigated. It has yet to be shown that there is a certain speed under which the cooling rate is low enough to permit the formation of compositional variations or favor a gradual change in composition as growth speed.

3.3.1.1 Nb$_2$O$_5$

The growth of Nb$_2$O$_5$ single crystals by any method has not been reported in the literature. There is one unpublished work by Kway and Feigelson (1983) mentioned that Nb$_2$O$_5$ fiber had been grown dimensionally stable by using the pull rate of 1.0 mm/min
and a feed rate of 0.17 mm/min, with the rotating of source rod 20 rpm. A platinum wire was used as the seed-rod.

For the LHPG instrument here at MRI, the capability of rotation is limited therefore, the growth rate of Nb$_2$O$_5$ single crystal needs to be adjusted several times to achieve the stable molten zone. Two sets of growth rate, slow pulling and fast pulling, were selected and are shown in Table 3-4. First, Nb$_2$O$_5$ crystal was grown by the slow pulling/feeding rate (20/20 mm/h). The growth was stable and yielded a long crystal of uniform diameter. However, the crystal consisted of a lot of facets with random orientations around the crystal. Growing single crystal with fast pulling/feeding rate is another option (2/1 mm/min). The resulting single crystal was smooth with uniform diameter and no facets were observed.

3.3.1.2 Nb$_2$O$_5$-TiO$_2$

According to the unstable molten zone, the growth of Nb$_2$O$_5$(1-x):TiO$_2$(x) required several adjustments of the growth rate until the stable shape of molten zone was accomplished. The pulling/feeding rate was set at 20/20 mm/h at the beginning of the growth and then the pulling rate was gradually increased till the stable molten zone was achieved. To produce the uniform diameters and uniform orientations of a single crystal, the minimum change of growth rate was required. Single crystals of Nb$_2$O$_5$(1-x):TiO$_2$(x) were successfully grown by using the growth rate varied from 20/20 mm/h to 35/20 mm/h.
Table 3-4: Growth rates of Nb₂O₅ single crystal fibers

<table>
<thead>
<tr>
<th>Growth Rate</th>
<th>Feed Rate</th>
<th>Pull Rate</th>
<th>Reduction Ratio</th>
<th>Molten Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow</td>
<td>20 mm/h</td>
<td>20 mm/hour</td>
<td>1</td>
<td>1500-1536°C</td>
</tr>
<tr>
<td>Fast</td>
<td>2 mm/min</td>
<td>1 mm/min</td>
<td>2</td>
<td>1493-1512°C</td>
</tr>
</tbody>
</table>
3.3.1.3 Nb$_2$O$_5$-SiO$_2$

Single crystal was first grown by slow speed (22/20 mm/h). Due to the difficulty in handling the molten zone, the second growth was carried out by fast speed (1.2/1 mm/min). By this condition, the resulting molten zone was stable yielding an uniform single crystal. Figure 3-19 shows the photograph of Nb$_2$O$_5$(0.92):SiO$_2$(0.08) single crystal grown with different growth rate.

3.3.1.4 Nb$_2$O$_5$-AL$_2$O$_3$

The growth of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) single crystals was achieved at the slow growth rate (22/20 mm/h) for all compositions. The stable molten zone was established and subsequently the uniform diameter single crystal fiber was grown. The summary of growth conditions of all compositions described above is given in Table 3-5.
Figure 3-19: Photograph of Nb$_2$O$_5$(0.92):SiO$_2$(0.08) single crystal; grown by different growth rate; (L) fast rate 1.2/1 mm/min, (R) slow rate 20/20 mm/h.
Table 3-5: Growth conditions of Nb₂O₅ based oxides single crystals

<table>
<thead>
<tr>
<th>Materials</th>
<th>Feed Rate</th>
<th>Pull Rate</th>
<th>Reduction Ratio</th>
<th>Molten Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>N95T5</td>
<td>20 mm/h</td>
<td>20 mm/h</td>
<td>1</td>
<td>1547-1562°C</td>
</tr>
<tr>
<td>N92T8t</td>
<td>25 mm/h</td>
<td>20 mm/h</td>
<td>1.25</td>
<td>1493-1512°C</td>
</tr>
<tr>
<td>N89T11</td>
<td>35 mm/h</td>
<td>20 mm/h</td>
<td>1.75</td>
<td>1530-1579°C</td>
</tr>
<tr>
<td>N95Si5</td>
<td>1.2 mm/min</td>
<td>1 mm/min</td>
<td>1.2</td>
<td>1548-1570°C</td>
</tr>
<tr>
<td>N92Si8</td>
<td>1.2 mm/min</td>
<td>1 mm/min</td>
<td>1.2</td>
<td>1551-1573°C</td>
</tr>
<tr>
<td>N89Si11</td>
<td>1.2 mm/min</td>
<td>1 mm/min</td>
<td>1.2</td>
<td>1560-1570°C</td>
</tr>
<tr>
<td>N95Al5</td>
<td>22 mm/h</td>
<td>20 mm/h</td>
<td>1.1</td>
<td>1545-1575°C</td>
</tr>
<tr>
<td>N92Al8</td>
<td>22 mm/h</td>
<td>20 mm/h</td>
<td>1.1</td>
<td>1547-1583°C</td>
</tr>
<tr>
<td>N89Al11</td>
<td>22 mm/h</td>
<td>20 mm/h</td>
<td>1.1</td>
<td>1565-1590°C</td>
</tr>
</tbody>
</table>
3.3.3 Crystal Structure and Orientation

Single crystal fibers can be characterized with regard to orientation, crystal defects and their chemical & physical properties by standard characterization techniques such as X-ray diffraction, optical microscopy, etc., although their small size makes handling and adaptation to conventional methods a more difficult task. Very small fibers do present significant handling problems in particular in the area of making physical property measurements.

3.3.1.1 Nb$_2$O$_5$

As grown single crystal was dark and shiny. After annealing in oxygen atmosphere, the dark area disappeared and the single crystal was transparent. These dark areas were caused by the reduction of Nb$^{5+}$ during the growth. To investigate the crystal structure, a piece of single crystal was crushed into powder for X-ray powder diffraction measurement. The XRD pattern of Nb$_2$O$_5$ single crystal reveals the monoclinic phase. In order to find the exact orientation of the growth axis, the single crystal was analyzed by the Laue x-ray reflection but unfortunately the strong background prevents the clear pattern. To simplify the determination of crystal orientations, the single crystals cut along the perpendicular plane to the growth axis and cut along the parallel plane to the growth axis were used for taking the XRD pattern. The results are shown in Fig. 3-20.
Figure 3-20: XRD pattern of Nb$_2$O$_5$ single crystal planes; (above) parallel plane to the growth axis, (below) perpendicular plane to the growth axis.
3.3.1.2 Nb₂O₅-TiO₂

The colorless transparent crystals (15-20 mm in length and 0.5 mm in diameter) were obtained for all compositions after annealing. The dark color of as grown crystals due to the reduction of Nb⁵⁺ to Nb⁴⁺ and probably also of Ti⁴⁺ to Ti³⁺ could easily be eliminated after annealing treatment, as shown in Fig. 3-21. Some difficulty in handling was encountered because of the presence of cracks, probably generated by the high temperature gradient and fast cooling (200-500 °C/min).

In order to determine the crystal structure, x-ray diffraction analysis was carried out on powder prepared by crushing the crystals. As illustrated in Figure 3-22, the XRD patterns of all three single crystals are identical indicating the same phase as of ceramics and the same structure except the lattice parameters may be varied.

3.3.1.3 Nb₂O₅-SiO₂

As mention earlier, the growth of Nb₂O₅(1-x):SiO₂(x) single crystals was stable and easy to control. The long and smooth single crystal fibers were obtained from all three compositions (average length ~30 mm), see Fig. 3-23. The reduction occurred in some areas but not much. The XRD patterns of crushed single crystal suggest the monoclinic phase of H-Nb₂O₅.
Figure 3-21: Nb₂O₅(0.89):TiO₂(0.11) single crystal; (above) as grown single crystal, (below) annealed single crystal.
Figure 3-22: XRD patterns of Nb2O5(1-x):TiO2(x) single crystals (crushed powder).
Figure 3-23: Photograph of as grown Nb$_2$O$_5$(1-x):SiO$_2$(x) single crystals.
Figure 3-24: Photograph of as grown Nb$_2$O$_5$\((1-x)\):Al$_2$O$_3$(x) single crystals.
3.3.1.4 Nb₂O₅-AL₂O₃

The dark color single crystals of Nb₂O₅(1-x):Al₂O₃(x) were obtained for all three compositions, as seen from Fig. 3-24. The colorless and transparent single crystals were obtained after heat treatment in oxygen atmosphere. The uniform diameter and long crystal growth resulted from the stable molten zone and growth rate. Characterized by x-ray diffraction pattern, single crystals show the single phase of monoclinic same as those of previous compositions.

3.4 Summary

In this chapter, the ceramic processing of Nb₂O₅ based oxides solid solutions prepared by the conventional mixed oxide method was described. The processing condition of each composition is summarized in Table 3-3. All ceramics show the presence of monoclinic phase of H-Nb₂O₅ as characterized by the x-ray diffraction method.

The single crystal fibers of each composition were successfully grown by the Laser-Heated Pedestal Growth (LHPG) technique. To obtain the good quality single crystal, the important factors such as the stability of molten zone and shape and the growth rate are required to accomplish the growth process. These parameters also influence the quality and appearance of the single crystal. The best growth conditions were obtained after several adjustments, as summarized in Table 3-4. The most common concern which was found in every growth is the reduction of Nb⁵⁺ that causes the dark color of as grown single crystals. Nevertheless, the dark color was easily eliminated by
annealing the crystals in oxygen atmosphere. The single crystals have the same phases (monoclinic) as of preform ceramics.

3.5 References

13. PDF card # 37-1468.


Chapter 4
DIELECTRIC PROPERTIES

This whole chapter was dedicated to the investigation of dielectric properties of niobate solid-solutions in both bulk ceramics and single crystal form. How the partial substitution additives change the dielectric behavior of pure niobate is of great interest.

4.1 Introduction

The solid state chemistry of Nb₂O₅ is very interesting due to the surprising complexity of its crystal structure. The structure contains Nb in many coordination environments, suggesting that many other metals may show solubility in significant proportion. The electrical and magnetic properties of Nb₂O₅ were found to be strongly affected by small variations of oxygen vacancies or dopants.1-3 The partial substitutions of some simple oxides are expected to dramatically change some of the intrinsic properties.

In that regard, we systematically explored the effects on the dielectric properties of bulk ceramics and single crystals of chemical additives selected from the list of elements considered fully acceptable in microelectronics processing environments. The list of such elements is highly restricted, e.g. Ti, Si, and Al.
4.2 Scope of Dielectric Measurements

4.2.1 Measurement System

4.2.1.1 Intermediate Temperatures (-180 to 180°C)

Dielectric measurements were performed on ceramic and single crystal fiber specimens using a multifrequency LCR meter. Measurements ranging from –180°C to 180°C were carried out in liquid N₂ cooled Delta Design environment chamber (Delta Design Inc., San Diego, CA) at selected frequencies in the range of 1 to 1000 kHz. Multifrequency LCR meter is a microprocessor-controlled impedance bridge which measures impedance of the specimen by supplying voltage signal (rms) of 1 V under unbias condition. LCR meter used in this experiment was HP 4284A (Hewlett-Packard, Palo Alto, CA). The impedance obtained by LCR meter is converted to capacitance and subsequently to dielectric constant (K) and loss tangent (tan δ) in a computer assisted set up. Stray capacitance and contact capacitance were compensated during calibration of the bridge. Heating and/or cooling rates were maintained at 2°C/min throughout all sets of experiments. Using a relay system, up to 8 samples could be simultaneously measured.

The various characteristic dependent dielectric properties were measured on both ceramics and single crystal fibers under various conditions; bias-field effect, annealing history effect, dopant type effect, etc.
4.2.1.2 Low Temperatures (10 to 300 K)

Dielectric measurements were carried out at low temperatures (10 to 300 K) using an automated measurement system. This system consisted of an LCR meter (HP-4284) and a Cryo-system which included a closed-cycle helium-cooled cryostat (Displex DS-202 and HC-2, APD cryogenics), a temperature controller (Model 330, Lakeshore), and a desktop computer. The specimen was being cooled or heated up at a typical cooling/heating rate of 2 K/min. The sample holder of this system is capable of 1 sample per run. To facilitate good electrical contact, a dot of air-dry silver was painted on the gold electrodes; fine gauge silver wire was also attached to both parallel sides of sample.

4.2.2 Sample Preparation and Electrode Geometries

For ceramic samples, disc-shaped samples were used for the dielectric measurements. Before electroding, the major faces of the discs were polished parallel with 12 µm silicon carbide powder, and geometries were recorded; typical dimensions of the disc were 10 mm in diameter and 1 mm in thickness. The polished specimens were annealed at 700°C for 3h in air in order to eliminate stresses introduced during polishing. Electrodes consisted of DC sputtered gold with air-dried silver applied to protect the gold and improve electrical contact.

The single crystal fiber samples were prepared from as-grown crystals in the form of parallel plate whose face normal is parallel to the growth direction. To observe anisotropic dielectric properties, single crystal fiber was cut into two pieces, one was side polished to a rectangular shape (parallel plane to the growth axis), and another one was
retained circular shape as grown and was polished parallel (perpendicular plane to the growth axis). The cross-sections of the samples were polished, finished at 3 µm alumina powder. All single crystal samples were annealed in oxygen at 1000°C for 5h before gold sputtered. The gold electrodes area was measured indirectly by photographing the electrodes area and comparing the weight with a graphic tracing paper (1x1 mesh) that was also photographed at the same magnification. Figure 4-1 shows samples of cut single crystals in perpendicular plane and parallel plane to the growth axis before annealing and after annealing. The as grown single crystal was dark because of the reduction of Nb$^{5+}$ however, after oxidizing, the dark color disappeared.

4.3 Dielectric Properties of Pure Niobate

4.3.1 Introduction

Crystalline ceramics, which are composed of transition metal oxides or glasses incorporating finite amounts of transition metal oxides, exhibit a-c losses that are governed by an electron or hole-type conduction mechanism.\(^4\) In the transition metal oxides, all or a portion of the d-shell electrons have been given off by the transition metal atom to the oxygen atom. With transition metal oxide ceramics such as niobium oxide (Nb$_2$O$_5$), the conductivity even at moderate temperature is governed by electronic conduction. This behavior has led to study by several investigators of Nb$_2$O$_5$ as an electrically conductive material.\(^5\text{-}^{10}\)
Figure 4-1: Single crystals were cut into perpendicular plane (⊥) and parallel plane (||) to the growth axis, comparing between before annealing (as grown single crystal) and after annealing.
In this section, the temperature dependence of dielectric constant (K) and dielectric loss (tan δ) of Nb₂O₅ ceramic and Nb₂O₅ single crystal fibers were measured to use as reference data before the investigation of the effect of additives in dielectric properties of Nb₂O₅-based oxide solid-solutions.

### 4.3.2 Ceramic of Nb₂O₅

Ceramic of Nb₂O₅ was prepared by conventional mixed oxide method, as described in chapter 3, with 98% theoretically density. The pellet was calcined at 1300°C for 24 h and was sintered at 1400°C for 3 h to assure the forming of single phase high temperature form. The powder X-ray diffraction pattern confirmed the single phase monoclinic system appearance.

The temperature dependence of dielectric constant (K) and dielectric loss (tan δ) of Nb₂O₅ ceramic is shown in Fig. 4-2. Pure Nb₂O₅ was conductive even at low temperature; the conductivity occurs at temperature > -70°C for frequency 1 kHz. At room temperature (1 MHz), the dielectric constant of Nb₂O₅ is roughly 33 and losses (~0.05) are of conductive in nature. The result shows some agreement with earlier studies that say Nb₂O₅ is a highly conductive material. These data will be used to compare with those of Nb₂O₅-based oxide solid-solutions.
Figure 4-2: Temperature dependence of dielectric constant (a) and dielectric loss (b) for Nb$_2$O$_5$ ceramic at various frequencies.
4.3.3 Single Crystal Fiber of Nb$_2$O$_5$

The single crystal fibers of Nb$_2$O$_5$ were grown by the LHPG technique as described in chapter 3. The dielectric properties of single crystals have been measured on both perpendicular and parallel plane to the growth direction as illustrated in Fig. 4-3 and 4-4 respectively. The dielectric properties of both planes show crystal orientation dependence or anisotropic dielectric properties. Dielectric constants (K) of the perpendicular plane are higher than those of the parallel plane. However, in the single crystal form, Nb$_2$O$_5$ is still highly conductive at lower measuring frequencies. This is the result of the fact that as a consequence of this kind of crystal chemistry Nb$^{5+}$ is partially reduced to Nb$^{4+}$ under high temperature of single crystal growth processing, as at high temperatures oxygen vacancies may be formed. The introduction of Nb$^{4+}$ introduced the electrical conductivity due to electrons by the defect reaction:

$$O_0 \rightarrow \frac{1}{2}O_2(g) + Nb^{4+} + e^-$$

This reduction was supported by the appearance of as grown single crystal of Nb$_2$O$_5$ which shows dark color which disappeared after annealing in oxygen environment.
Figure 4-3: Dielectric properties of pure niobate single crystal in perpendicular plane, as a function of temperature, for eight frequencies; (a), (b) dielectric constant (K) and dielectric loss tangent (tan δ) of perpendicular plane; showing high conductive materials.
Figure 4-4: Dielectric properties of pure niobate single crystal in parallel plane, as a function of temperature, for eight frequencies; (a), (b) dielectric constant ($K$) and dielectric loss tangent ($\tan \delta$) of parallel plane; showing high conductive materials.
Table 4-1: Summary of the dielectric properties of Nb₂O₅ in various forms at 20°C

<table>
<thead>
<tr>
<th>Material</th>
<th>$K_{(1 \text{ MHz})}$</th>
<th>$\tan \delta_{(1 \text{ MHz})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb₂O₅ ceramic</td>
<td>33</td>
<td>0.05</td>
</tr>
<tr>
<td>Nb₂O₅ single crystal (⊥ plane)</td>
<td>140</td>
<td>0.02</td>
</tr>
<tr>
<td>Nb₂O₅ single crystal (∥ plane)</td>
<td>60</td>
<td>0.002</td>
</tr>
</tbody>
</table>
4.4 Dielectric Properties of Nb$_2$O$_5$(1-x):TiO$_2$(x)

4.4.1 Introduction

As seen from the dielectric measurements of pure Nb$_2$O$_5$, the results at low frequencies were in agreement with the previous reports$^{5-10}$ that claimed Nb$_2$O$_5$ as a conductive material. It behaves like dielectric material solely at low temperature and high frequencies. It is of great interest to investigate the influences of small substituents to the dielectric properties of Nb$_2$O$_5$. Cava et al.$^{11}$ (1995) had reported the dielectric constant of Ta$_2$O$_5$ can be greatly enhanced (from 35 to 130) with the additional of a small amount of TiO$_2$. Both Nb$_2$O$_5$ and Ta$_2$O$_5$ have the complex chemistry and Nb$^{5+}$ has same valency as Ta$^{5+}$. Consequently, the small addition of TiO$_2$ in Nb$_2$O$_5$ has been expected to increase the dielectric constant of Nb$_2$O$_5$ as well.

4.4.2 Ceramic of Nb$_2$O$_5$(1-x):TiO$_2$(x)

4.4.2.1 Dielectric Constant and Dielectric Loss

Three niobium titanates studied in this work are Nb$_2$O$_5$(1-x):TiO$_2$(x), at $x=0.05,0.08,0.11$. The temperature dependence of the dielectric constants (K) of the three niobium titanates at various frequencies is summarized in Figure 4-5 to 4-7, covering the full temperature range of the dielectric measurements. Figure 4-5(a) shows the data for Nb$_2$O$_5$(0.95):TiO$_2$(0.05) which clearly represent the frequency dependence of the dielectric constants. The maximum K is shifted to higher temperature while the
measurement frequencies are increased. At low frequency, 1 kHz, the sample conductivity increases at temperature about 110 °C. As Ti substitutions are increased to x=0.08 (Fig. 4-6(a)), the enhancement of dielectric constants are observed at the same time the sample conductivity enhances for low frequency measurements at approximately 130 °C. The data clearly shows the improvement of the dielectric properties with partial substitutions of Ti (high frequency data). The same effects are shown in Nb2O5(0.89): TiO2(0.11) (Fig. 4-7(a)). The summary of the dielectric constants of all three niobium titanates at 1 MHz is presented in Table 4-2.

The temperature and frequency dependence of the dielectric losses are shown in Figure 4-5(b)-4-7(b). All the niobium titanates studied in this research seem to exhibit some kind of relaxation behavior and hence influencing the dielectric properties at low frequencies. Also some contribution to the dielectric loss values may be due to the presence of oxygen vacancies and possibly presences of Nb3+, Nb4+ in these samples.

As Ti content is increased, the dielectric loss, tan δ is increased. This is a result from the fact that Ti4+ is easily partially reduced to Ti3+ under normal ceramic processing conditions in these materials, as at high temperatures oxygen vacancies may be formed. The introduction of Ti3+ increases tan δ through the introduction of electrical conductivity due to electrons by the defect reaction:

\[ \text{O}_6 \rightarrow \frac{1}{2} \text{O}_2(g) + \text{Ti}^{3+} + e^- \]

The part of the dielectric losses observed in the materials could be due to the presence of defect structure. The concentration of defect structure depends upon the mode and quantity of ionic site substitutions and doping, non-stoichiometry as well as
adherence to perfect crystallinity in the case of crystals and some porosity, grain boundaries, etc. in the case of ceramics. Very careful control of defect structure, doping levels and proper processing could lead to further lowering in the loss values.

Figure 4-5(b)-4-7(b) also show that the temperature of dielectric loss peak increases with increasing frequency. This common behavior indicates that all three materials may also have some kind of relaxation process. The common picture of the relaxation behavior in dielectric properties can be summarized as follows:  

(1) existence of a non-Debye dielectric dispersion in a large frequency range, usually at low frequencies (10 Hz-10 MHz), around and below the peak temperature of the real part of dielectric permittivity ($T_{\text{max}}$)

(2) $T_{\text{max}}$ is a function of frequency and increases with frequency.

(3) A sudden increment of the dielectric losses below $T_{\text{max}}$; the dielectric losses show a frequency dispersion which is opposite to that of the dielectric constant.
Figure 4-5: Temperature dependence of dielectric constant (a) and dielectric loss (b) for Nb$_2$O$_5$(0.95):TiO$_2$(0.05) ceramic at various frequencies.
Figure 4-6: Temperature dependence of dielectric constant (a) and dielectric loss (b) for Nb$_2$O$_5$(0.92):TiO$_2$(0.08) ceramic at various frequencies.
Figure 4-7: Temperature dependence of dielectric constant (a) and dielectric loss (b) for Nb$_2$O$_5$(0.89):TiO$_2$(0.11) ceramic at various frequencies.
Table 4-2: Summary of the dielectric properties at 1 MHz of Nb$_2$O$_5$(1-x): TiO$_2$(x) ceramics

<table>
<thead>
<tr>
<th>Material (Nb$_2$O$<em>5$)$</em>{(1-x)}$:TiO$_2$(x)</th>
<th>100°C</th>
<th>20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{(1 \text{ MHz})}$</td>
<td>$\tan \delta_{(1 \text{ MHz})}$</td>
</tr>
<tr>
<td>X = 0.05</td>
<td>179.3</td>
<td>0.031</td>
</tr>
<tr>
<td>X = 0.08</td>
<td>248.1</td>
<td>0.054</td>
</tr>
<tr>
<td>X = 0.11</td>
<td>239.6</td>
<td>0.033</td>
</tr>
</tbody>
</table>
4.4.2.2 Relaxation Mechanism Analysis

4.4.2.2.1 Arrhenius Relationship

The low-frequency dielectric loss phenomena are analyzed by the Arrhenius formalism\textsuperscript{13-14}, which is valid for Debye-like loss mechanisms:

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right)$$  \hspace{1cm} (4.1)

where $k$ is the Boltzmann’s constant ($8.314 \times 10^{-5}$ eV/K), $T$ the temperature at which the relaxation peak has a maximum, and $\tau_0$ the time constant.

It follows from this equation that for a given angular frequency ($\omega = 2\pi f$), a peak in the imaginary part of the dielectric constant will occur at a temperature ($T_m$) where $\omega \tau = 1$. The activation energy ($E_a$) can be calculated from the slope of the Arrhenius plot of $\ln \tau$ versus $1/T_m$. The pre-exponential factor ($\tau_0$) is related to the nature of the mechanism responsible for the relaxation phenomenon. For data in which the loss peak temperature ($T_m$) is known for several frequencies, the relaxation time ($\tau$) is the reciprocal of the measurement frequency ($\omega$). The imaginary parts of the dielectric constant ($\varepsilon''$) versus temperature and the corresponding Arrhenius plots, for frequencies between 100 Hz and 1 MHz, of $\text{Nb}_2\text{O}_5(1-x):\text{TiO}_2(x)$ at $x = 0.05, 0.08, 0.11$ are presented in Figure 4-8, 4-10, and 4-12 respectively. At $x = 0.05,$ Fig. 4-8, two relaxation phenomena are clearly visible in the lower frequency data; two maxima are observed at the 100 Hz-100 kHz data, which gradually coalesce into one maximum at frequency 1 MHz. The Arrhenius plot of $x=0.05,$ Fig. 4-9, can conform to two straight lines at low and high temperature. The activation
energy ($E_a$) values calculated from the low temperature data set and high temperature data sets were 0.17 eV and 0.67 eV with the pre-exponential factors ($\tau_o$) of $7.2 \times 10^{-11}$ seconds and $1.0 \times 10^{-17}$ seconds respectively. The reciprocal of the time constant of low temperature mode compares well with the frequency of the lattice for ionic solids over the frequency range of $10^{11}-10^{13}$ Hz. Theses parameters are indicative of ionic jump or dipole relaxation. The reciprocal of the time constant of high temperature mode falls in the frequency of electronic contribution to the polarization which is the common behavior of Nb$_2$O$_5$ conductivity at high temperature.

With increasing Ti substitutions, Nb$_2$O$_5$(0.92):TiO$_2$(0.08) presents only one relaxation phenomenon with the activation energy ($E_a$) of 0.68 eV and the pre-exponential factors ($\tau_o$) of $2.9 \times 10^{-18}$ seconds, as illustrated in Fig 4-10 and 4-11. For Nb$_2$O$_5$(0.89):TiO$_2$(0.11), two relaxation phenomena are observed at frequency 100 Hz and become one relaxation phenomenon at higher frequencies, Fig. 4-12. The activation energy ($E_a$) calculates from the entire data set of Nb$_2$O$_5$(0.89):TiO$_2$(0.11) was 0.48 eV with a pre-exponential factor of $8.1 \times 10^{-16}$ seconds. The reason for high activation energy of these substances will be investigated in further study.
Figure 4-8: Temperature dependent imaginary parts (K") of the dielectric constant for Nb$_2$O$_5$(0.95):TiO$_2$(0.05).
**Figure 4-9:** Arrhenius plot, logarithm of the relaxation time versus reciprocal temperature of the peak (from Fig. 4-8) showing an Arrhenius relationship.
Figure 4-10: Temperature dependent imaginary parts (K") of the dielectric constant for Nb$_2$O$_3$(0.92):TiO$_2$(0.08).
Figure 4-11: Arrhenius plot, logarithm of the relaxation time versus reciprocal temperature of the peak (from Fig. 4-10) showing an Arrhenius relationship.
Figure 4-12: Temperature dependent imaginary parts ($K''$) of the dielectric constant for $\text{Nb}_2\text{O}_5(0.89):\text{TiO}_2(0.11)$. 
Figure 4-13: Arrhenius plot, logarithm of the relaxation time versus reciprocal temperature of the peak (from Fig. 4-12) showing an Arrhenius relationship.
Table 4-3: The analysis of dielectric loss relaxation process by the Arrhenius relationship of Nb$_2$O$_5$(1-x):TiO$_2$(x) ceramics

<table>
<thead>
<tr>
<th>Relaxation Parameters</th>
<th>N95T5 Low T mode</th>
<th>N95T5 High T mode</th>
<th>N92T8 High T mode</th>
<th>N89T11 High T mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_0$ (s)</td>
<td>7.2x10$^{-11}$</td>
<td>1x10$^{-17}$</td>
<td>2.9x10$^{-18}$</td>
<td>8.1x10$^{-16}$</td>
</tr>
<tr>
<td>$E_a$ (eV)</td>
<td>0.17</td>
<td>0.67</td>
<td>0.68</td>
<td>0.48</td>
</tr>
</tbody>
</table>
4.4.2.3 Effect of Oxidation

Both Nb$_2$O$_5$ and TiO$_2$ are oxides of complicated stoichiometry and Nb$_2$O$_5$ in particular can exist in one crystalline phase within a wide O/Nb range.$^{17}$ Thus, the resistivity of Nb$_2$O$_5$ (as well as that of TiO$_2$) is strongly affected by even small variations in the oxygen vacancy concentration$^{18}$ which may already be introduced by experimental uncertainty$^{19}$ during the processing. The relatively high dielectric losses in materials suggest the presence of high concentration of oxygen vacancies. Nevertheless, the control of annealing condition such as in O$_2$ condition may reduce the concentration of oxygen vacancies.

The proof of the above assumption was carried on one sample of Nb$_2$O$_5$(1-x):TiO$_2$(x) ceramic. N92T8 pellet, after polishing, was annealed in air atmosphere at 700°C for 3 hours before sputtering electrodes. The dielectric measurement was taken and then the electrodes were removed before the second heat treatment. This time, N92T8 pellet was annealed in O$_2$ atmosphere furnace at 1000°C for 5 hours before the dielectric properties were measured.

Figure 4-14 shows the result of annealing history effect on the dielectric properties of N92T8. The dielectric loss, tan δ, was roughly reduced by 15%. The relaxation phenomena was presented as the same nature, only the temperature of maximum dielectric loss peak was shifted to lower temperature for the sample annealed in O$_2$ furnace. These results show that annealing causes some but not big change in the dielectric properties mainly because of the lower oxidation rate occurred in the dense ceramic. Only a small oxidations might have occurred at the surface of the sample.
Figure 4-14: Dielectric constant (K) and tan δ of Nb$_2$O$_5$(0.92):TiO$_2$(0.08) ceramics at different annealing conditions; (a) air annealing at 700°C for 3 hours, (b) oxygen annealing at 1000°C for 5 hours.
Table 4-4: Summary of dielectric properties (K and tan δ) of Nb$_2$O$_5$(0.92):TiO$_2$(0.08) ceramics at different annealing conditions

<table>
<thead>
<tr>
<th></th>
<th>K (20°C)</th>
<th>tan δ (20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 kHz</td>
<td>1 MHz</td>
</tr>
<tr>
<td>Air 700°C/3h</td>
<td>235</td>
<td>138</td>
</tr>
<tr>
<td>O$_2$ 1000°C/5h</td>
<td>200</td>
<td>120</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>K (50°C)</th>
<th>tan δ (50°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 kHz</td>
<td>1 MHz</td>
</tr>
<tr>
<td>Air 700°C/3h</td>
<td>250</td>
<td>180</td>
</tr>
<tr>
<td>O$_2$ 1000°C/5h</td>
<td>220</td>
<td>160</td>
</tr>
</tbody>
</table>
4.4.2.4 Bias Field Effect

Strong nonlinear effect under dc electric field is a characteristic of polar dielectrics, and has found many applications.\textsuperscript{20-21} Recently, a series of microwave devices, high Q resonant circuits are being developed by combining electric-field agile nonlinear dielectrics with superconducting oxides.\textsuperscript{22} The demand of a dielectric material with both high electric field tunability and very low dielectric loss is captivated by the potential uses in tunable microwave devices such as filters and phase shifter. Many materials so called “quantum paraelectric” such as SrTiO$_3$,\textsuperscript{23-25} KTaO$_3$,\textsuperscript{25,26-27} and CaTiO$_3$\textsuperscript{28} have been extensively studied the dielectric behaviors under dc electric field.

The measurements were conducted by applying a small ac signal of 1 Vrms amplitude and 10 kHz frequency while the direct-current (dc) field was swept from positive bias to negative bias at each constant temperature. The direct-current (dc) voltage is applied to the samples and a blocking circuit was adopted to separate the high dc voltage and LCR meters. The highest bias field applied was 20 kV/cm due to the limitation of the blocking circuit. At each measuring temperature, the sample was allowed to be equilibrated for 15 min before the field dependences of dielectric constant and loss were recorded.

Figure 4-15 shows the bias field dependence of the dielectric constant and dielectric loss of each composition at room temperature. The dielectric properties change significantly with dc bias field. At composition x=5, the dielectric constant decreases continuously with the increasing of dc bias field. When Ti contents were increased, x = 8 and 11, the dielectric constant increases at small electric field and then drops gradually
with the increasing of dc bias field. Obviously, all dielectric behaviors exhibit nonlinear dielectric under dc bias field.

The tunability of the dielectric constant was calculated by using the expression:

$$Tunability(\%) = \frac{K(E_0) - K(E)}{K(E_0)} \times 100\%$$  \[(4.2)\]

where \(E_0\) is the starting electric field, generally taking \(E_0 = 0\) kV/cm, and \(E\) is the electric field at which we calculate tunability. The calculated tunability of each composition was depicted in Fig. 4-16. The \(\text{Nb}_2\text{O}_5(0.95):\text{TiO}_2(0.05)\) presented the highest tunability, 8.5% at 10 kV/cm.

The possible interpretation of dielectric nonlinearity is related to polar nanoregions. Polar nanoregion is defined as nanometer scale regions with parallel oriented polarization, where they consist of each other acting as a giant dipole with slow relaxation frequency.\(^{29-30}\) The polar nanoregion is susceptible to environmental disturbance and apt to redirect to external field vector even under weak signal level.

A polar glass model is adopted to rationalize the results shown in Fig. 4-16. The external dc bias can change the height of potential barrier that must be overcome by the dipoles when turning over. When a small dc bias field is applied to the ceramics, the potential barrier becomes lower for the dipoles with their directions opposite to the external bias field, so these dipoles obtain much more transition opportunities. Meanwhile the dipoles with the same direction as the external bias field still have certain transition probabilities. This results in the increase of the dielectric constant at lower bias field. With the increasing of bias field, the potential barrier becomes deeper and deeper for the dipoles that have the same direction as the bias field, and their transition
probabilities decline more and more. These dipoles then make less contribution to the dielectric response consequently leads to the decrease of dielectric constant.

The hysteresis loop occurred in the cycle of sweep bias was believed to be intrinsic hysteretic. If the material is in polar or a ferroelectric state then we have some kind of anti-phase boundaries or the domain walls to deal with. They may, or may not, have to move under the influence of the applied field. Many factors will affect the mobility of the domains, but the most critical are probably defect dipoles, grain boundaries, and maybe porosity. Once a defect dipole is moved or flipped, or a wall moves from one grain to another, the mobility is slightly changed so that the system will not return to the exact state in which it began. If the material is not ferroelectric then one would assume that the defects and anything else will migrate under the influence of an electric field.

Figure 4-17 shows the dc bias property of Nb$_2$O$_5$(0.92):TiO$_2$(0.08) ceramic at various temperatures. It is obviously seen that the ceramic exhibits different dielectric nonlinearity at different temperatures. As temperature was lower, the response to the external field was less. This can be explained by the reason that most dipoles are slow dipoles or frozen dipoles.

The exact analysis of the results has been further complicated due to the presence of multiple relaxation phenomena (and their origin). More detailed studies are needed to analyse the contribution from individual factors. But, it is concluded that polar regions/cluster in these materials are present due to the occurrence of various Magneli phases of monoclinic symmetry (point group 2 and m). These conclusions will further be discussed and supported in the following chapter also.
Figure 4-15: Bias field dependence of dielectric constant (a) and dielectric loss (tan δ) of Nb$_2$O$_5$(1-x):TiO$_2$(x) at 10 kHz and room temperature.
Figure 4-16: Bias field dependence of the tunability (%) of $\text{Nb}_2\text{O}_5(1-x):\text{TiO}_2(x)$ at 10 kHz and room temperature.
Figure 4-17: Bias field dependence of dielectric properties of Nb$_2$O$_5$(0.92):TiO$_2$(0.08) ceramic at various temperatures.
4.4.3 Single Crystal Fiber of Nb$_2$O$_5$(1-x):TiO$_2$(x)

4.4.3.1 Sample Preparation

The Laser-Heated Pedestal growth (LHPG) method was used to grow single crystals of Nb$_2$O$_5$(1-x):TiO$_2$(x) solid-solutions. After growth, single crystal fibers were treated by oxygen annealing at 1000°C for 5 hours. Fibers were cut into 2 pieces for dielectric measurement (area vectors parallel and perpendicular to the growth axis). Each single crystal piece was polished with fine 3 µm of Al$_2$O$_3$ powder, then was sputtered gold electrode using DC magnetron sputtering (SCD 050, Bal-Tec Inc.). Any excess electrode on the sides of the samples was gently sanded off with fine sandpaper.

4.4.3.2 Anisotropy Dielectric Properties

The temperature and frequency dependencies of the relative dielectric constant (K) and dielectric loss tangent (tan δ) were measured over the temperature range –180°C to 180°C and the frequency range 1 kHz to 1 MHz. The single crystals of each composition have been measured for the dielectric properties on both parallel plane and perpendicular plane in relation to the growth direction. The high dielectric constants, (K on the order of 1000 at room temperature), dependent on the crystal orientation are clearly seen from the Nb$_2$O$_5$(0.95): TiO$_2$(0.05) and the Nb$_2$O$_5$(0.89):TiO$_2$(0.11) single crystals [Fig.4-17 and Fig.4-18]. The high dielectric constant was observed in perpendicular plane samples. The frequency dispersions of dielectric loss tangent are observed in all samples indicating two relaxation processes and perhaps a third at higher
temperatures. As Ti content increasing, the relaxation processes dominating and also shifting to the higher temperature. The relaxation data for the Nb$_2$O$_5$(0.95):TiO$_2$(0.05) (perpendicular plane) was analyzed to demonstrate the relaxation analysis by Arrhenius law and Vogel-Fulcher relation, discussed in the following section.

From Fig. 4-3, 4-4, (the dielectric properties of pure niobate single crystal), one can see that a low atomic concentration of titanium (0.05-0.11 at. mol %) evidently suppressed the conductivity behavior of pure niobate single crystal. Subsequent annealing in oxidizing atmosphere will further decrease the extrinsic losses in the samples.
Figure 4-18: Temperature dependence of dielectric constant (a) and dielectric loss (b) for Nb$_2$O$_5$(0.95):TiO$_2$(0.05) single crystal (perpendicular plane to the growth direction) at various frequencies.
Figure 4-19: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$ (0.95):TiO$_2$ (0.05) single crystal (parallel plane to the growth direction) at various frequencies.
Figure 4-20: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.89):TiO$_2$(0.11) single crystal (perpendicular plane to the growth direction) at various frequencies.
Figure 4-21: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.89):TiO$_2$(0.11) single crystal (parallel plane to the growth direction) at various frequencies.
4.4.3.3 Relaxation Mechanism Analysis

Relaxation is often better understood from the changes in the dielectric loss (dielectric absorption, \(K''\))\(^{31}\), which are shown in Fig. 4-22 as a function of temperature and frequency. One set of peaks can be clearly distinguished between −180°C and −50°C while the second set of peaks occurred at higher temperature between −50°C and 100°C.

According to the Debye model\(^{13}\), the reciprocal frequency of each peak gives the relaxation time, \(\tau\) (in second). (The Debye model usually refers to the frequency domain, but it is also valid for the temperature domain.) When the logarithms of the relaxation times are plotted versus the reciprocal of the peak temperature, a set of straight line is observed, as shown in Fig.4-23. The relaxation fits an Arrhenius relationship, where the slope is equal to the activation energy (\(E_a\)), as shown in Eq. (4.1).

The activation energy \(E_a = 0.15\) eV and \(\tau_0 = 1.2\times10^{-11}\) s (a frequency of 0.83x \(10^{11}\) Hz) are given for the low temperature mode and \(E_a = 0.65\) eV and \(\tau_0 = 1.0\times10^{-16}\) s (a frequency of \(10^{16}\) Hz) for the high temperature mode, as summarized in Table 4-5. The reciprocal of the time constant of low temperature region compares well with the frequency of the lattice for ionic solids over the frequency range of \(10^{11}-10^{13}\) Hz. These parameters are indicative of ionic jump or dipole relaxation\(^{12,13}\).

From Table 4-5, it can be seen that the parameter for high temperature, \(\tau_0 = 1.0\times10^{-16}\) s (corresponding to a frequency \(10^{16}\) Hz), seems to be too high for the system. Due to this reason, we have tried to fit the Vogel-Fulcher relation\(^{32}\) for high temperature relaxation. Many complications can affect a Debye-type process, such as a distribution of activation energies and correlations between individual relaxors. Such complications are
well known to occur in spin and dipolar glass$^{33}$ According to the superparaelectric model, a dielectric relaxation occurs due to thermally activated polarization reversal between equivalent variants.$^{27}$ This model describes the dynamics of the polar microregions in relation to temperature. The Vogel-Fulcher analysis is the basis of the dipole-glass model.$^{34}$ Freezing of the dipoles results from cooperative interactions between moments on the nanometer scale. The frequency dispersion of the real permittivity maximum can be described by the Vogel-Fulcher relation:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k(T - T_f)}\right) \quad (4.3)$$

where $T_f$ is a freezing temperature. Near $T_f$, the long time relaxation reflects slow dynamics. The system is characterized by a slow down of a normal domain structure: a frozen polar state is reached at temperatures which are sufficiently low. Almost the same fitting quality is obtained from the Vogel-Fulcher relation due to the high ratio between the peak temperature and the freezing temperature. The fitting parameters also include in Table 4-5.

$\text{Nb}_2\text{O}_5(0.92):\text{TiO}_2(0.08)$ and $\text{Nb}_2\text{O}_5(0.89):\text{TiO}_2(0.11)$ single crystal fibers show one relaxation mode in this temperature range. The same analyses were applied to all single crystal samples. The complete calculated parameters of all compositions are summarized in Table 4-5.
Figure 4-22: Temperature dependent imaginary parts (K") of dielectric constant for Nb_2O_5(0.95):TiO_2(0.05) single crystal (parallel plane), clearly showing two relaxation processes occurred in this temperature range.
Figure 4-23: Corresponding Arrhenius and Vogel-Fulcher plots: The logarithms of the relaxation times are plotted versus the reciprocal of the peak temperature (from Fig. 4-22), to analyze the relaxation mechanism by Arrhenius law and Vogel-Fulcher relationship.
Table 4-5: The analysis parameters of dielectric loss relaxation process by the Arrhenius law and the Vogel-Fulcher relationship of Nb$_2$O$_3$(1-x):TiO$_2$(x) single crystals.

<table>
<thead>
<tr>
<th>Analysis Model</th>
<th>Arrhenius</th>
<th>Vogel-Fulcher</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ (eV)</td>
<td>$\tau_0$ (s)</td>
</tr>
<tr>
<td>N95T5</td>
<td></td>
<td>plane (Low T mode)</td>
</tr>
<tr>
<td>(High T mode)</td>
<td>0.65</td>
<td>$1.0 \times 10^{-16}$</td>
</tr>
<tr>
<td>$\perp$ plane (Low T mode)</td>
<td>0.14</td>
<td>$4.5 \times 10^{-12}$</td>
</tr>
<tr>
<td>(High T mode)</td>
<td>0.51</td>
<td>$1.6 \times 10^{-14}$</td>
</tr>
<tr>
<td>N92T8</td>
<td></td>
<td>plane</td>
</tr>
<tr>
<td>$\perp$ plane</td>
<td>0.38</td>
<td>$1.9 \times 10^{-14}$</td>
</tr>
<tr>
<td>N89T11</td>
<td></td>
<td>plane</td>
</tr>
<tr>
<td>$\perp$ plane</td>
<td>0.42</td>
<td>$9.6 \times 10^{-14}$</td>
</tr>
</tbody>
</table>
4.4.3.4 Effect of Oxidation

In the Ti-containing oxides, the variation of the Ti ions valence and consequently the appearance and disappearance of the oxygen vacancies in the sample play an important role in the dielectric response. Most observations had been done in Ti-containing perovskite-type ABO$_3$ ionic oxides. Maglione et al. reported dielectric relaxation phenomena in a number of perovskite materials containing Ti, such as in BaTiO$_3$, CaTiO$_3$, PbTiO$_3$-based systems. They found that the dielectric relaxation was closely related to the oxygen vacancies in the samples. Zhi Yu et al. reported the frequency dependent dielectric peaks in Bi and La doped SrTiO$_3$ systems can be gradually decreased and finally eliminated in oxidizing atmosphere. This gives the clear evidence that the relaxing species are related to oxygen vacancies in Bi or La doped SrTiO$_3$. Shulman et al. investigated the dielectric anomalies in bismuth titanate (Bi$_4$Ti$_3$O$_{12}$), a perovskite-layer structure, and proposed that the oxygen ions are responsible for low-temperature ion-jump relaxation.

In recently investigated Nb$_2$O$_5$(1-x):TiO$_2$(x) solid-solution systems, the crystal structure is monoclinic and Ti content is very small when compared to the perovskite systems described above. Therefore the effect of oxidation on dielectric anomalies may not show dramatic changes but it is expected to present some changes.

In order to compare the dielectric behavior, first the N95T5 single crystal (perpendicular plane) was annealed in O$_2$ atmosphere at 1000°C for 2 different times, 5 hours and 24 hours. The dielectric constant and dielectric loss of each annealing condition was measured and the results are shown in Fig. 4-24 and Fig. 4-25 respectively.
Figure 4-24: Temperature dependent dielectric constant (K) of N95T5 single crystal (perpendicular plane) at different annealing condition.
Figure 4-25: Temperature dependent dielectric loss (tan δ) of N95T5 single crystal (perpendicular plane) at different annealing conditions.
As seen from the results, the dielectric constant peaks were decreased as annealing time was increased. Same result was obtained in dielectric loss data. These indicate that the peaks in dielectric properties are most probably related to the oxygen content. These results agree with the results of annealing effect in ceramics as shown in Fig. 4-14.

The dielectric relaxations of two different annealing conditions show the same behavior. Inserting the single crystal sample in oxidizing atmosphere for 24 hours in regular furnace is probably not have enough pressure to put oxygen ions into crystal structure due to high density of crystal structure. Therefore, the N95T5 single crystal (perpendicular plane) after removing electrode was annealed one more time in Hot Isostatic Pressing (HIP). This process was expected to introduce more oxygen ions into the samples. A commercial HIP (HIP-3000, Leco Corp. /TEM Press Div.) was used to apply pressures of up to 3000 psi while heating the ceramics to 1100°C in argon – oxygen atmosphere for 2 hours. The dielectric properties of N95T5 single crystal after HIP process are shown in Fig. 4-26. The results show dramatically decreasing of dielectric constant peak and dielectric loss peak when compared to those of sample annealed in regular O₂ furnace.

To investigate whether the relaxation occurred in this sample is the characteristic of oxygen-ion-jump mechanism or not, the imaginary part of dielectric constant (K″) was plotted against temperature to find the temperature of maximum peak (Tₘ) in each annealing condition, as seen in Fig. 4-27. Two relaxation processes were clearly presented in both cases but the Tₘ of sample annealed by HIP process is shifting to higher temperature. The Arrhenius analysis was applied to calculate the relaxation
parameters as illustrated in Fig. 4-28. The reciprocal of the time constants ($\tau_0$) of low
temperature region of both samples fall in the same relaxation frequency range ($10^{11}$-$10^{13}$ Hz) which implied the same relaxation mechanism occurred in both samples. The
activation energy ($E_a$) for the relaxation can be viewed as an energy barrier that separates the two positions of oxygen-ion-jump. Sample annealed in HIP process has higher activation energy that means the occurrence of ion jumping between two positions is less likely.

Annealing in HIP process can reduce the high concentration of oxygen vacancies. As the oxygen vacancy is less, the oxygen ion jumping is decreased. These conclusions support that the oxygen ions are responsible for the low-temperature ion-jump relaxation.
Figure 4-26: Temperature dependent dielectric constant (a) and dielectric loss (b) of N95T5 single crystal (perpendicular plane) after annealing in HIP process.
Figure 4-27: Temperature dependent imaginary part (K") of dielectric constant of N95T5 single crystal (perpendicular plane) after annealing in different conditions.
Figure 4-28: Corresponding Arrhenius plot of N95T5 single crystal (perpendicular plane) after annealing in different conditions.
4.5 Dielectric Properties of Nb$_2$O$_5$(1-x):SiO$_2$(x)

4.5.1 Introduction

The previous sections have recently shown that the dielectric constant of Nb$_2$O$_5$ can be increased dramatically through small substitution of TiO$_2$. In ceramic of Nb$_2$O$_5$(1-x):TiO$_2$(x), the dielectric constant increased as the Ti content increased. While in single crystals, the dielectric properties were highly crystal orientation dependent.

Further investigation of dielectric properties of Nb$_2$O$_5$ based solid-solutions was conducted on SiO$_2$ doping, best known for compatibility with microelectronics processing. SiO$_2$ is the crystal structure of highly covalent bond which is known for the stability whereas TiO$_2$ is the crystal structure of highly ionic bond and Ti valences play an important role to the dielectric properties of solid-solution. The SiO$_2$ doped Nb$_2$O$_5$ ceramics and single crystals were expected to show a marked difference in behavior from the TiO$_2$ doped Nb$_2$O$_5$. One previous work$^{37}$ studied the substitution of SiO$_2$ into Ta$_2$O$_5$ polycrystalline ceramic. The ceramics of Ta$_2$O$_5$(1-x):SiO$_2$(x) were reported to have enhanced dielectric constant (to a maximum of $K \approx 45$ at $x = 0.10$) over that of Ta$_2$O$_5$ ($K \approx 30$).
4.5.2 Ceramic of Nb$_2$O$_5$(1-x):SiO$_2$(x)

4.5.2.1 Dielectric Constant and Dielectric Loss

Ceramics of Nb$_2$O$_5$(1-x):SiO$_2$(x) at x=5, 8, and 11 mol% were prepared by the same method as described earlier. The Nb$_2$O$_5$(1-x):SiO$_2$(x) powders were made by mixing the appropriate molar amounts of Nb$_2$O$_5$ (99.995%) and SiO$_2$ (99.99%). These were thoroughly ball-milled for 24 h and then calcined at 1300°C for 24 h. Pellets were preformed by uniaxial pressing and then followed by cold isostatic pressing. The green ceramics were sintered at 1400°C for 3 h after a low-temperature binder burnout step.

The dielectric properties of ceramic of each composition were measured in the temperature range of 180°C to -180°C and the measurements were taken at frequencies, 1 kHz, 10 kHz, 100 kHz, and 1 MHz. Results of dielectric properties of Nb$_2$O$_5$(1-x):SiO$_2$(x) at x=5, 8, and 11 mol% are shown in Fig. 4-29, 4-30, and 4-31 respectively.

The dielectric behaviors of Nb$_2$O$_5$(1-x):SiO$_2$(x) solid-solutions show the different characteristic from those of Nb$_2$O$_5$(1-x):TiO$_2$(x) solid-solutions as follows;

(a) The dielectric constant (K) is decreased as the Si content is increased whereas the opposite trend was obtained for Nb$_2$O$_5$(1-x):TiO$_2$(x) solid-solutions. At composition x = 0.05, the ceramic yields the highest dielectric constant, K= 207 at 20°C. The summarized results of dielectric parameters of each composition are listed in Table 4-6. The dielectric loss (tan δ) of Nb$_2$O$_5$(1-x):SiO$_2$(x) solid-
solutions is less than those of Nb₂O₅(1-x):TiO₂(x) solid-solutions compared at the same temperature and frequency.

(b) The variation of K with temperatures of Nb₂O₅(1-x):SiO₂(x) solid-solutions is much less than those of Nb₂O₅(1-x):TiO₂(x) solid-solutions. Especially at temperature range of 0-100°C, the dielectric constants of Nb₂O₅(1-x):SiO₂(x) solid-solutions is approximately constant with temperature. The conductivity of low frequency (1 kHz) begins to occur at temperature higher than 100°C for all compositions.

(c) The frequency dependent dielectric constant or dielectric dispersion of Nb₂O₅(1-x):SiO₂(x) solid-solutions was observed at lower temperature range and one relaxation was shown within these measurement temperatures. At temperature higher than 0°C, the dielectric dispersion is less or almost no frequency dependent dielectric constant.

Nevertheless, the doping of SiO₂ enhances the dielectric properties of Nb₂O₅ as same as in the case of TiO₂. The dielectric constant of these solid-solutions has been dramatically increased to a higher level than those of the end members; Nb₂O₅ (K ~ 33) and SiO₂ (K ~ 3-4), as seen in Table 4-6.
Figure 4-29: Temperature dependent dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.95):SiO$_2$(0.05) ceramic.
Figure 4-30: Temperature dependent dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.92):SiO$_2$(0.08) ceramic.
Figure 4-31: Temperature dependent dielectric constant (a) and dielectric loss (b) of Nb₂O₅(0.89):SiO₂(0.11) ceramic.
Table 4-6: Summary of the dielectric properties at 1 MHz of Nb$_2$O$_5$(1-x): SiO$_2$(x) ceramics

<table>
<thead>
<tr>
<th>Material (Nb$_2$O$<em>5$)$</em>{(1-x)}$: SiO$_2$(x)</th>
<th>100 °C</th>
<th>20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{(1\ MHz)}$</td>
<td>$\tan \delta_{(1\ MHz)}$</td>
</tr>
<tr>
<td>X = 0.05</td>
<td>209</td>
<td>0.02</td>
</tr>
<tr>
<td>X = 0.08</td>
<td>128</td>
<td>0.01</td>
</tr>
<tr>
<td>X = 0.11</td>
<td>97</td>
<td>0.02</td>
</tr>
</tbody>
</table>
4.5.2.2 Sintering Effect

To investigate the relationship of the dielectric properties with the processing conditions, Nb$_2$O$_5$(0.89):SiO$_2$(0.11) ceramics were prepared under five different sintering conditions (designated A, B, C, D, and E respectively). The samples’ abbreviations, their calcinations, sintering conditions, as well as the relative density of ceramics are summarized in Table 4-7.

Figure 4-32 represents the X-ray powder diffraction patterns of samples A, B, C, D, and E, corresponding to different processing conditions. The XRD patterns of sample A, B, C, D, and E show the H-Nb$_2$O$_5$ monoclinic phase, in agreement with the published data on phase. The mixing of small amount of Magneli’ phases was observed in all samples which show strong peak in sample A (sintering 1350°C/3h).

Figure 4-33 shows SEM micrographs of sintered surface of sample A, B, C, D, and E. The microstructures were characterized by grains of various sizes and morphologies. For sample sintered at 1350°C (A), the grain size was small and revealed intragranular porosity. Higher sintering temperature enables grain growth and reductions of porosity (B, C, D, and E). Longer sintering time, the elongated grains were developed, about 10 µm in sample C then increasing to 20 µm in sample E. The grain structure becomes anisotropic, although the density was improved. The abnormal grain growth as seen from sample D and E was originated from the Nb-rich liquid phase.
Table 4-7: Dielectric properties of Nb$_2$O$_5$(0.89):SiO$_2$(0.11) ceramics under different sintering conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination ($^\circ$C/h)</th>
<th>Sintering ($^\circ$C/h)</th>
<th>Annealing ($^\circ$C/h)</th>
<th>Relative density (%)</th>
<th>$K_{1 \text{ MHz}}$ 20$^\circ$C</th>
<th>tan $\delta_{1 \text{ MHz}}$ 20$^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1300/24</td>
<td>1350/3</td>
<td>700/3</td>
<td>91.2</td>
<td>83.2</td>
<td>0.070</td>
</tr>
<tr>
<td>B</td>
<td>1300/24</td>
<td>1400/24</td>
<td>700/3</td>
<td>95.5</td>
<td>92.2</td>
<td>0.036</td>
</tr>
<tr>
<td>C</td>
<td>1300/24</td>
<td>1400/48</td>
<td>700/3</td>
<td>96.1</td>
<td>99.1</td>
<td>0.037</td>
</tr>
<tr>
<td>D</td>
<td>1300/24</td>
<td>1400/72</td>
<td>700/3</td>
<td>96.3</td>
<td>100.5</td>
<td>0.039</td>
</tr>
<tr>
<td>E</td>
<td>1300/24</td>
<td>1400/96</td>
<td>700/3</td>
<td>96.0</td>
<td>94.7</td>
<td>0.033</td>
</tr>
</tbody>
</table>
Figure 4-32: XRD patterns of samples A, B, C, D, and E, corresponding to different processing conditions.
Figure 4-33: SEM micrograph of Nb$_2$O$_5$(0.89):SiO$_2$(0.11) ceramics prepared under different sintering conditions. (A) 1350°C/3h, (B) 1400°C/24h, (C) 1400°C/48h, (D) 1400°C/72h, (E) 1400°C/96h.
Table 4-7 summarizes the dielectric constant, loss tangent of \( \text{Nb}_2\text{O}_5(0.89):\text{SiO}_2(0.11) \) ceramics at 1 MHz, in correspondence to different sintering conditions. The temperature dependence of dielectric constant and loss tangent between -180 and 180°C at 10 kHz and 1 MHz are shown in Fig. 4-34 and Fig. 4-35 respectively. The results obtained at 10 kHz and 1 MHz are similar in nature.

Inspection of data in Table 4-7, Fig. 4-34 and Fig. 4-35 reveals an apparent trend of enhancement of dielectric constant via increasing sintering temperature from 1350°C to 1400°C. The conductivity is vividly reduced as considered from dielectric loss data. As can be seen from Fig. 4-33, sample sintered at 1350°C for 3 hours shows large porosity which results in the low density as well as causes a high conductivity in dielectric results. After the sample was sintered at 1400°C, the prolonged sintering time causes a slight increase in dielectric constant and then a decrease of the dielectric constant was observed in sample sintered at 1400°C for 96 hours. It can be seen that ceramic sintering at 1400°C for 96 hours (sample E) having large and elongated grains, the dielectric constants may be larger in some directions than that of the ceramics having smaller grain size and uniform grain structures, due to the anisotropy of physical properties. The longer sintering time causes the distribution of grains to be non-uniform, which may be responsible to the slightly increasing of the loss tangent (0.036-0.039).

The data from samples sintering under different conditions suggest that the difference in dielectric behavior is due to factors such as ceramic density, the change of microstructure shapes, and the presence of abnormal grain growth or elongated grains.
Figure 4-34: Temperature dependent dielectric constant (a) and dielectric loss (b) of Nb₂O₅(0.89):SiO₂(0.11) ceramics under different sintering conditions, at 10 kHz.
Figure 4-35: Temperature dependent dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.89):SiO$_2$(0.11) ceramics under different sintering conditions, at 1 MHz.
4.5.2.3 Low Temperature Dielectric Properties

Recently, this solid solution has been investigated for dielectric properties at various frequencies and temperatures. Doping with small amounts of simple oxides such as TiO$_2$ or SiO$_2$ caused the dielectric constant of solid solutions to increase to a higher level than those of the end-members. Frequency dispersion in the dielectric constant, as well as in the dielectric loss factor, revealed a very interesting relaxation mechanism. To clearly investigate this mechanism, the relaxor-like dielectric characteristics were carefully measured at cryogenic temperatures (10–300 K) where strong relaxation was presented. The frequencies used were 0.1, 0.2, 0.4, 1, 2, 4, 10, 20, 40, 100, 200, 400, 1000 kHz. All frequencies were not necessarily used for every measurement, but only those demanded data for fitting in equations.

The modified Debye model known as a Cole-Cole plot was employed to analyze the relaxation parameters and distribution of relaxation time. Furthermore, if the relaxation process is governed by thermally activated motion, the activation energy and corresponding relaxation time can be calculated by an Arrhenius relationship.

Illustrations of the frequency dependence of the dielectric responses known as dielectric constant (K) and dissipation factor (tan $\delta$) are shown in Figs. 4-36. The frequency dependence of dielectric permittivity curves demonstrate typical relaxation behavior, with the magnitude of dielectric permittivity decreasing with increasing frequency and maximal shifting to higher temperatures. Three modes of relaxation mechanisms are observed within the entire range of the experiment, suggesting the various relaxation species that cause dispersion.
Figure 4-36: Low temperature dependent dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.92):SiO$_2$(0.08) ceramic at various frequencies.
The reduction of Nb$^{+5}$ species is possible during heat treatment, yielding reduced valence such as Nb$^{+4}$ and Nb$^{+3}$. It has been suggested that electrons sometimes create dielectric relaxation by moving like thermally activated charged particles, i.e., by “hopping”. This “electron hopping effect” creates the donor-type extrinsic defect. Substitutions of Si ions in the Nb ion site contribute the acceptor-type defect; when the acceptor-type defect is combined with the donor-type extrinsic defect as describe above, the dipole moments are generated and induce high permittivity of this solid solution. Nb$^{+5}$ ion hopping also results in dielectric loss, as shown in Fig. 4-36(b).

4.5.2.4 Relaxation Mechanism Analysis

4.5.2.4.1 Cole-Cole Analysis

An understanding of the observed shapes of the dielectric loss peaks and dielectric constant dispersion can be obtained by using the analysis first proposed by Cole and Cole (1941).\textsuperscript{39} If the experimental results of $\varepsilon''$ versus $\varepsilon'$ are represented on a Cole-Cole plot, a distribution of relaxation times causes the center of the semicircular arc to assume a position below the $\varepsilon'$-axis. Cole and Cole showed that in their empirical description of the distribution of relaxation times, the complex permittivity may be expressed as

$$
\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+ (j\omega\tau)^{1-a}}
$$

(4.4)
where $\varepsilon^*$ is defined by $\varepsilon^* = \varepsilon' - j\varepsilon''$, and $j = \sqrt{-1}$. $\varepsilon''$ is the imaginary part of the dielectric constant and is also commonly referred to as the loss factor or loss index of the dielectric material. A plot of the imaginary part of the permittivity (or of the dielectric constant, $\varepsilon''$) versus the real part can yield important information such as the values of $\varepsilon_s$ and $\varepsilon_\infty$ (the limiting values of the dielectric constant at frequencies sufficiently below and above the particular loss mechanism) and the distribution of relaxation times.

For a pure Debye relaxation, a plot of $\varepsilon''$ versus $\varepsilon'$ results in a semicircular arc above the $\varepsilon'$-axis, with intersections along the $\varepsilon'$-axis at points corresponding to $\varepsilon_s$ and $\varepsilon_\infty$. If a distribution of relaxation time is included in the relaxation mechanism, this arc is tilted with respect to the $\varepsilon'$-axis. The tilt angle is defined as $\alpha \pi/2$, and the tilt parameter ($\alpha$) is related to the distribution of relaxation times. Typical Cole-Cole plots at various temperatures of an Nb$_2$O$_5$(0.92):SiO$_2$(0.08) sample are shown in Fig. 4-37. The data were fitted to the Cole-Cole equation with the least-squares approach using Matlab program, yielding the fitting parameters, $\varepsilon_\infty$, $\varepsilon_s$, $\alpha$, and $\tau$. All parameters are summarized in Table 4-8.
Figure 4-37: Cole-Cole plot of $\varepsilon''$ vs $\varepsilon'$ at various temperatures of Nb$_2$O$_3$(0.92):SiO$_2$(0.08) ceramic.
Table 4-8: Dielectric quantities derived from Cole-Cole plot

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\varepsilon_s$</th>
<th>$\varepsilon_\infty$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>125.63</td>
<td>38.63</td>
<td>0.659</td>
</tr>
<tr>
<td>100</td>
<td>129.50</td>
<td>33.98</td>
<td>0.776</td>
</tr>
<tr>
<td>80</td>
<td>144.10</td>
<td>32.25</td>
<td>0.818</td>
</tr>
<tr>
<td>60</td>
<td>202.20</td>
<td>31.64</td>
<td>0.860</td>
</tr>
<tr>
<td>40</td>
<td>105.94</td>
<td>32.07</td>
<td>0.875</td>
</tr>
<tr>
<td>20</td>
<td>60.14</td>
<td>32.97</td>
<td>0.873</td>
</tr>
</tbody>
</table>
With decreasing temperature, $\alpha$ is increased, indicating departure from the single relaxation mechanism. At 150 K, strong dielectric dispersion was observed in Fig. 4-36; this region is called “Mode I” relaxation. The experimental data is well-fitted to the Cole-Cole arc plot, but the distribution of relaxation time ($\alpha$) is quite large. Large $\alpha$ probably arises because of the random dipole fields between the cluster moment and the distribution of cluster size effect. When the temperature is lowered to 100 K, the $\alpha$ value is larger because this region is near the onset of “Mode II” relaxation. Consequently, the merging of two relaxation mechanism yields a larger distribution. Analysis of the Cole-Cole plot at 80 K shows the nature of the “Mode II” relaxation mechanism. Substituted Si ion is probably the relaxation specie, but this explanation needs further study. At 60 K, this region combines the relaxation mechanisms of Mode II and Mode III. As the temperature is reduced to near freezing, all dynamic clusters freeze and all relaxation mechanisms shut down. The dielectric responses are almost frequency-independent, resulting in the inapplicability of Cole-Cole fitting. As seen in Fig.4-37, the lower the temperature, the lower the frequency dependence of the dielectric response.

Analyses of Cole-Cole plots show the larger distribution of relaxation time when the temperature is lowered. All relaxation mechanisms shut down when the measurement temperature reaches the freezing point.

### 4.5.2.4.2 Arrhenius Relationship

Only Mode I relaxation has been analyzed by the Arrhenius relationship due to the most clearly peak values. It follows from the Arrhenius equation that for a given
angular frequency \((\omega = 2\pi f)\), a peak in the imaginary part of the dielectric constant will occur at a temperature \((T_m)\) where \(\omega \tau = 1\), as shown in Fig. 4-38. The activation energy \((E_a)\) can be calculated from the slope of the Arrhenius plot of \(\ln \tau\) versus \(1/T_m\). The pre-exponential factor \((\tau_o)\) is related to the nature of the mechanism responsible for the relaxation phenomenon. The frequency dispersion of the imaginary part of the permittivity maximum revealed close agreement with an Arrhenius relationship, as seen in Fig. 4-39. An activation energy of 0.16 eV and a pre-exponential factor of \(10^{-12}\) s were calculated for \(\text{Nb}_2\text{O}_5(0.92):\text{SiO}_2(0.08)\).

### 4.5.2.5 Bias Field Effect

The ceramic of \(\text{Nb}_2\text{O}_5(0.92):\text{SiO}_2(0.08)\), while being held in cryogenic temperature, was measured the dc electric field dependence of dielectric constant and dielectric loss by sweeping from 0 kV/cm to 20 kV/cm then sweeping back to negative field. The dc electric field dependence of dielectric constant and dielectric loss at various temperatures were illustrated in Fig. 4-40. The results show the nonlinear dielectric response to the field but not as strong as those found in single crystal sample.
Figure 4-38: Temperature and frequency-dependent imaginary parts of dielectric constant of Nb$_2$O$_5$(0.92):SiO$_2$(0.08) ceramic.
Figure 4-39: Corresponding Arrhenius plot for Nb$_2$O$_5$(0.92):SiO$_2$(0.08) relaxation Mode I.

\[ E_a = 0.16 \text{ eV} \]
\[ \tau_0 = 4.2 \times 10^{-12} \text{ s} \]
Figure 4-40: Bias field dependence of dielectric properties of Nb$_2$O$_5$(0.92):SiO$_2$(0.08) ceramic at various temperatures.
4.5.3 Single Crystal Fiber of Nb$_2$O$_5$(1-x):SiO$_2$(x)

4.5.3.1 Sample Preparation

The single crystal of Nb$_2$O$_5$(1-x):SiO$_2$(x), x = 0.05, 0.08, and 0.11, were grown by the LHPG technique. The molten zones of these solid-solution are more stable than those of Nb$_2$O$_5$(1-x):TiO$_2$(x). The reduction of Nb$^{5+}$ occurred during the growth, obviously seen from shiny dark color of as grown single crystal fibers. After annealing in O$_2$ furnace at 1000°C for 5 hours, the dark color disappeared. Each single crystal was cut in different plane to the growth direction, perpendicular and parallel, for anisotropic properties measurement. Each piece of single crystal was polished with fine 3 µm of Al$_2$O$_3$ powder, and then gold electrode was sputtered.

4.5.3.2 Anisotropy Dielectric Properties

High dielectric constants (on the order of 1000) were observed in single crystals of Nb$_2$O$_5$(1-x):SiO$_2$(x) cut in perpendicular plane to the growth axis, as illustrated in Fig. 4-41, Fig. 4-43, and Fig. 4-45, respectively. Low dielectric constant (on the order of 10) was observed in single crystals cut in parallel plane to the growth axis, as seen from Fig. 4-42, Fig. 4-44, and Fig. 4-46, respectively. The value of dielectric constant decreased as the content of SiO$_2$ increased, showing the same agreement with those of ceramics. Within the measurement temperature range, two relaxation processes were present in the frequency dependence of dielectric loss for all samples.
Figure 4-41: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.95):SiO$_2$(0.05) single crystal (perpendicular plane to the growth direction) at various frequencies.
Figure 4-42: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.95):SiO$_2$(0.05) single crystal (parallel plane to the growth direction) at various frequencies.
Figure 4-43: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.92):SiO$_2$(0.08) single crystal (perpendicular plane to the growth direction) at various frequencies.
Figure 4-44: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.92):SiO$_2$(0.08) single crystal (parallel plane to the growth direction) at various frequencies.
Figure 4-45: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.89):SiO$_2$(0.11) single crystal (perpendicular plane to the growth direction) at various frequencies.
Figure 4-46: Temperature dependence of dielectric constant (a) and dielectric loss (b) of $\text{Nb}_2\text{O}_5(0.89):\text{SiO}_2(0.11)$ single crystal (parallel plane to the growth direction) at various frequencies.
4.6 Dielectric Properties of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x)

4.6.1 Introduction

Al$_2$O$_3$ was known to be a very stable oxide and it has fabrication compatibility with the microelectronic manufacturing. Small substitutions of Al$_2$O$_3$ were found to enhance the dielectric properties of bulk Ta$_2$O$_5$.\textsuperscript{40} It was reported that bulk polycrystalline ceramics of Ta$_2$O$_5$(1-x):Al$_2$O$_3$(x), for small value of $x$ (~0.05-0.2), have somewhat increased dielectric constant over that of Ta$_2$O$_5$ (K~25-30), reaching a maximum of ~40 for $x$ near 0.1 even though the K of Al$_2$O$_3$ itself is only 8. There was also a report of enhanced dielectric constant in thin film of Ta$_2$O$_5$(1-x):Al$_2$O$_3$(x).\textsuperscript{41} A high dielectric constant of 42.8 was obtained for Ta$_2$O$_5$(0.9):Al$_2$O$_3$(0.1) thin film. Those characteristics have made Al$_2$O$_3$ an attractive candidate for studying the doping effect in Nb$_2$O$_5$ system.

4.6.2 Ceramic of Nb$_2$O$_5$(1-x): Al$_2$O$_3$ (x)

4.6.2.1 Dielectric Constant and Dielectric Loss

Ceramics of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) at $x$=5, 8, and 11 mol% were prepared by the same method as previous experiment. The Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) powders were made by mixing the appropriate molar amounts of Nb$_2$O$_5$ (99.995%) and Al$_2$O$_3$ (99.99%). These were thoroughly ball-milled for 24 h and then calcined at 1350°C for 24 h. Pellets were preformed by uniaxial pressing and then followed by cold isostatic pressing. The green ceramics were sintered at 1450°C for 3 h after a low-temperature binder burnout step.
The dielectric properties of ceramic of each composition were measured in the temperature range of 180°C to -180°C and the measurements were taken at frequencies, 1 kHz, 10 kHz, 100 kHz, and 1 MHz. Results of dielectric properties of \( \text{Nb}_2\text{O}_5(1-x):\text{Al}_2\text{O}_3(x) \) at \( x=5, 8, \) and 11 mol% are shown in Fig. 4-47, 4-48, and 4-49 respectively.

The dielectric constant of \( \text{Nb}_2\text{O}_5(1-x):\text{Al}_2\text{O}_3(x) \) decreased as the amount of \( \text{Al}_2\text{O}_3 \) increased, see summary in Table 4-9. Nevertheless, all compositions yielded a higher dielectric constant than those of end-members. The dielectric loss data (\( \tan \delta \)) shows the expected relaxation mechanism. All three compositions exhibit only 1 mechanism of relaxation within these measurement temperature ranges. The relaxation mechanism seems to occur at higher temperature range as the content of \( \text{Al}_2\text{O}_3 \) increased.
Figure 4-47: Temperature dependent dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.95):Al$_2$O$_3$(0.05) ceramic at various frequencies.
Figure 4-48: Temperature dependent dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.92):Al$_2$O$_3$(0.08) ceramic at various frequencies.
Figure 4-49: Temperature dependent dielectric constant (a) and dielectric loss (b) of Nb₂O₅(0.89):Al₂O₃(0.11) ceramic at various frequencies.
Table 4-9: Summary of the dielectric properties at 1 MHz of Nb$_2$O$_5$(1-x): Al$_2$O$_3$(x) ceramics

<table>
<thead>
<tr>
<th>Material</th>
<th>100 °C</th>
<th>20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Nb$_2$O$<em>5$)$</em>{(1-x)}$: Al$_2$O$_3$(x)</td>
<td>$K_{(1 MHz)}$</td>
<td>tan $\delta_{(1 MHz)}$</td>
</tr>
<tr>
<td>X = 0.05</td>
<td>167</td>
<td>0.05</td>
</tr>
<tr>
<td>X = 0.08</td>
<td>103</td>
<td>0.13</td>
</tr>
</tbody>
</table>
4.6.2.2 Relaxation Mechanism Analysis

A relaxation mechanism was observed for each composition of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) ceramic within the measurement temperature range. The relaxation mechanism of Nb$_2$O$_5$(0.95):Al$_2$O$_3$(0.05) occurred at lower temperature range than those of Nb$_2$O$_5$(0.92):Al$_2$O$_3$(0.08) and Nb$_2$O$_5$(0.89):Al$_2$O$_3$(0.11). In order to have more precise value of $T_m$ for calculating the relaxation parameters, the Nb$_2$O$_5$(0.95):Al$_2$O$_3$(0.05) ceramic was also measured the dielectric properties in cryo stat system; temperature range 10-300 K. Figure 4-50 shows the plot of temperature dependent imaginary part ($\varepsilon''$) and the corresponding calculation the relaxation parameters from the Arrhenius’s law.

4.6.2.3 Bias Field Effect

The Nb$_2$O$_5$(0.92):Al$_2$O$_3$(0.08) ceramic was measured the dc electric field dependence of dielectric constant and dielectric loss by sweeping from 0 kV/cm to 20 kV/cm then sweeping back to negative field. The measurement frequency was 10 kHz and the experiment was operated in cryogenic temperature. The results are shown in Fig.4-51. The tunability (%) was calculated as previously described, as illustrated in Fig. 4-52.

At high temperatures, the dielectric constants were increased with increasing bias field, which was called the negative tunability. As the temperature was lower, the tunability decreased until becoming zero at one temperature, 180 K. There is no dielectric response to the electric field at temperatures lower than 180 K.
Figure 4.50: (a) Temperature and frequency-dependent imaginary parts of dielectric constant of $\text{Nb}_2\text{O}_3(0.95):\text{Al}_2\text{O}_3(0.05)$ ceramic and (b) the corresponding Arrhenius plot.
Figure 4-51: Bias field dependence of dielectric properties of Nb$_2$O$_5$(0.92):Al$_2$O$_3$(0.08) ceramic at various temperatures
Figure 4-52: Bias field dependence of the tunability (%) of Nb$_2$O$_5$(0.92):Al$_2$O$_3$(0.08) at 10 kHz.
4.6.3  Single Crystal Fiber of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x)

4.6.3.1  Sample Preparation

The Laser-Heated Pedestal growth (LHPG) method was used to grow single crystals of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) solid-solutions. After growth, single crystal fibers were treated by oxygen annealing at 1000°C for 5 hours. Fibers were cut into 2 pieces for dielectric measurement (area vectors parallel and perpendicular to the growth axis). Each single crystal piece was polished with fine 3 µm of Al$_2$O$_3$ powder, then gold electrode was sputtered using DC magnetron sputtering (SCD 050, Bal-Tec Inc.). Any excess electrode on the sides of the samples was gently sanded off with fine sandpaper.

4.6.3.2  Anisotropy Dielectric Properties

High anisotropic dielectric properties of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) Single crystals shows the same agreement with the results of Nb$_2$O$_5$(1-x):TiO$_2$(x) and Nb$_2$O$_5$(1-x):SiO$_2$(x) single crystals, as illustrated in Fig. 4-53 through Fig. 4-58. The perpendicular plane of single crystals shows high dielectric constants whereas the parallel plan shows low dielectric constants.

A relaxation mechanism was observed for each single crystal sample and has similar nature as occurred in ceramic samples.
Figure 4-53: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb_2O_5(0.95):Al_2O_3(0.05) single crystal (perpendicular plane to the growth direction) at various frequencies.
Figure 4-54: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.95):Al$_2$O$_3$(0.05) single crystal (parallel plane to the growth direction) at various frequencies.
Figure 4-55: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.92):Al$_2$O$_3$(0.08) single crystal (perpendicular plane to the growth direction) at various frequencies.
Figure 4-56: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb$_2$O$_5$(0.92):Al$_2$O$_3$(0.08) single crystal (parallel plane to the growth direction) at various frequencies.
Figure 4-57: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb₂O₅(0.89):Al₂O₃(0.11) single crystal (perpendicular plane to the growth direction) at various frequencies.
Figure 4-58: Temperature dependence of dielectric constant (a) and dielectric loss (b) of Nb₂O₅(0.89):Al₂O₃(0.11) single crystal (parallel plane to the growth direction) at various frequencies.
4.7 Summary

The dielectric properties of ceramic samples of Nb$_2$O$_5$(1-x):TiO$_2$(x), Nb$_2$O$_5$(1-x):SiO$_2$(x), Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) at x = 0.05, 0.08, 0.11, have been measured at intermediate frequency range of 1 kHz-1 MHz. By varying the content of additive TiO$_2$, the dielectric constants for Nb$_2$O$_5$(1-x):TiO$_2$(x) are considerably enhanced over that of pure Nb$_2$O$_5$ although the crystal structures of these ceramics are strongly related to that of H-Nb$_2$O$_5$ (monoclinic). The data taken as a whole suggest that the present materials, if considered for applications, would represent a compromise among the ideal requirements of high K. Their relatively high dielectric loss values in some cases suggest the presence of high concentration of oxygen vacancies in these samples. Nevertheless, the control of annealing condition such as in O$_2$ could reduce the high concentration of oxygen vacancies.

The temperature dependencies of the dielectric constants at various frequencies of all three samples show the dielectric dispersion. The frequency dependent dielectric losses are observed, suggesting several relaxation phenomena. Some of the relaxation related effects slow down at higher frequencies ~GHz (see Fig. 2-3) therefore, these compositions could be useful for high frequency applications also.

The single crystals of Nb$_2$O$_5$(1-x):TiO$_2$, Nb$_2$O$_5$(1-x):SiO$_2$(x), Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) at x = 0.05, 0.08, 0.11, are grown successfully by the LHPG technique. The dielectric properties are strongly dependent on the direction of crystal orientation indicating high anisotropic nature of the single crystals. The high dielectric constant (on the order of 1000) was observed in the direction of growth axis (single crystal cut along
the perpendicular plane to the growth axis) whereas the low dielectric constant (on the order of 10 or 100) was observed in 90° direction to the growth axis (single crystal cut along the parallel plane to the growth axis). All selected additives, TiO₂, SiO₂, and Al₂O₃, led to a decrease of the losses of Nb₂O₅: Frequency dependent maxima in tan δ are observed in all three compositions suggesting the relaxation phenomena in these materials. The relaxation parameters were analyzed using the approaches such as Debye, Arrhenius, Cole-Cole, and Vogel-Fulcher relationship. The analysis was indicative of ionic jump or dipole relaxations as associated mechanism at low temperatures. The relaxation at high temperature mode is assumed to be involved by the existence of polar clusters which will be investigated in the next chapter.
4.8 References


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Chapter 5

POLAR CLUSTERS INVESTIGATIONS

This chapter is intended to investigate the existence of polar-cluster nanoregions in single crystals of Nb$_2$O$_5$ based oxides. It is assumed that the presence of polar clusters causes the high dielectric constant and the distribution of cluster sizes along with defect dipoles that generates the relaxation in these samples.

5.1 Introduction

There is a large volume of literatures suggesting the existence of polar-cluster nanoregions to describe the phenomena of strong frequency dispersion of the dielectric maxima in relaxor materials.\textsuperscript{1-5} It is believed that a small variation in polar cluster size can lead to a wide dielectric dispersion covering several frequency decades. Thomas\textsuperscript{2} has presented a theoretical framework for PMN in terms of the contributions made by individual NbO$_6$ and MgO$_6$ octahedra which he believed to be polar units. Bell\textsuperscript{3} utilized a phenomenological approach to calculate the dielectric properties of relaxors using Cross’s superparaelectric model.\textsuperscript{6} Initially, relaxors were treated as (i) an ensemble of independent, identical, monosized superparaelectric clusters, and subsequently, (ii) a distribution in size of the clusters, (iii) temperature-dependent cluster size, and (iv) dipolar cluster interaction are supposed. The results from these scenarios suggested that a
model involving a distribution of sizes and a temperature-dependent size gives the best qualitative fit to the relaxor behavior.

Quantum paraelectrics like KTaO₃ and SrTiO₃ are well known to undergo transitions into ferroelectric low temperature phases in the presence of small amount of polar impurities. The polar clusters dispersed in a paraelectric matrix resembles, in many aspects, the superparamagnetic clusters in spin glasses, consequently, Cross suggested that the polar clusters are superparaelectric with the polarization vectors thermally fluctuating between equivalent potential wells. It has been proposed, in analogy with the cluster model of spin glasses that the polar clusters behave like large superparaelectric dipole moments. The broad distribution of relaxation times for cluster orientations originates from the distribution of the potential barriers separating different orientational state. The superparaelectric model based on the assumption of independent clusters cannot explain, however, the appearance of long-range order with the change of the material composition or due to an applied external field.

This chapter tries to model quantitatively the dielectric response of relaxation in single crystal of Nb₂O₅ based solid solution which was assumed to be originated from the presence of small amounts of polar impurities. The polar impurities were treated as polar clusters. The influence of the cluster size dispersion is one assumption. Thus, the data of dc bias field dependence of the dielectric constant has been analyzed by the modified Devonshire relation including a cluster term giving the fitted parameters: cluster sizes distribution and their polar cluster polarization. The details of the approach are given in section 5.3.3.
5.2 Experimental Procedure

The experiments were performed on a single-crystal sample of Nb$_2$O$_5$(0.95):TiO$_2$(0.05). Complex dielectric constant measurements were made using an automated measurement system. This system consisted of an LCR meter (HP 4284A) with the ac field of 1 V/mm. Measurements were made at temperatures between -180 and 180°C at a rate of 2°C/min.

Tunability measurements were conducted in the same system with the addition of a voltage source (TREK 610) and a high voltage blocking circuit that isolated the LCR meter from the high voltages applied to the sample. A dc voltage was applied to the sample. At each measuring temperature the sample was allowed to maintain thermal equilibrium for 15 min before the field dependence of the dielectric constant and loss data were recorded.

5.3 Results and Discussion

5.3.1 Temperature Dependence of the Dielectric Constant and Loss

Temperature dependence of the dielectric constant (K) and dielectric loss (tan δ) as a function of frequency for Nb$_2$O$_5$(0.95):TiO$_2$(0.05) single crystal sample is shown in Fig. 5-1. From -180 to 180°C, K increases continuously with sharp drop at temperature about 120°C. This single crystal yields very high dielectric constant when compares to the conventional dielectric materials. However, there is a loss tan δ peak with a frequency dispersive behavior. Two relaxation modes were clearly observed within the
measurement temperature ranges. The analyses of relaxation mechanism were done in the previous chapter. The strong dispersion which exists in a large frequency range implies that the relaxation process involved is not a Debye type.

5.3.2 Field Dependence of the dielectric constant and loss

The dc electric-field dependence of the $K$ and $\tan \delta$ around the temperatures of dispersion range is illustrated in Fig. 5-2(a) and 5-2(b), respectively. It clearly shows that both $K$ and $\tan \delta$ decrease with increasing electric field from 0 to 20 kV/cm. For example, at $T = 60^\circ C$, the dielectric maximum ($K = 352$) at 20 kV/cm is much lower than the value ($K = 871$) at zero electric field.

The tunability is defined as the change in the dielectric constant under an applied electric field relative to the initial unbiased value, i.e.:

$$Tunability(\%) = \left( \frac{K(E_o) - K(E)}{K(E_o)} \right) \times 100\%$$  \hspace{1cm} (5.1)

where $E_o = 0$ kV/cm and $E$ is the electric field at which we calculate the tunability. The bias field dependence of the tunability at various temperatures is shown in Fig. 5-3. At higher temperature, the tunability is higher than those of lower temperature. The high value of 59% tunability was obtained when the sample was applied an electric field of 20 kV/cm at 60$^\circ$C.
Figure 5-1: Temperature dependence of dielectric constant (a) and dielectric loss (b) for Nb$_2$O$_5$(0.95):TiO$_2$(0.05) single crystal (perpendicular plane to the growth direction) at various frequencies.
Figure 5-2: Bias field dependence of dielectric constant (a) and dielectric loss (tan δ) of Nb₂O₅(0.95):TiO₂(0.05) single crystal at 10 kHz.
Figure 5-3: Bias field dependence of the tunability (%) of Nb$_2$O$_5$(0.95):TiO$_2$(0.05) single crystal at 10 kHz.
From the results, it was obvious that the polar clusters exist in this sample. As temperature was decreased, these polar clusters were possibly frozen (and some may coalesce to form the bigger size) that reduces the agility to respond to the external field.

5.3.3 Fits to the Modified Devonshire Relation

According to the Devonshire’s thermodynamic theory, the dielectric behavior in a paraelectric state under low dc electric-fields can be expressed as\(^8,9\)

\[
\varepsilon(E) = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4
\]  \hspace{1cm} (5.2)

\(\varepsilon_1\) is the linear dielectric constant and \(\varepsilon_{2,3}\) are the first and second nonlinear dielectric constant respectively; and \(E\) is dc electric field. The Eq. (5.2) has been widely adopted to analyze the electric-field dependence of the dielectric behavior of nonlinear dielectrics.\(^4,10-11\) However, the poor fits of \(\varepsilon(E)\) vs \(E\) is not enough to explain the semibell-shaped curves in Fig.5-4. The deviation from Eq. (5.2) implies that there is an excess contribution beyond the paraelectric matrix.

In addition to a background contribution coming from the intrinsic behavior, it was found that a polar-cluster contribution-Langevin-type polar-cluster contribution term has to be taken into account.\(^4\) By means of the Langevin-type approach, the total polarization of a cluster system can be expressed as\(^3\)

\[
P_c = P_r \tanh\left(\frac{P_r L' E}{2k_B T}\right)
\]  \hspace{1cm} (5.3)
with the effective polarization of one cluster $P_r$, the cluster size $L$, the electric field $E$, and Boltzmann’s constant $k_B$. By assuming one cluster gives contribution, 

\[
(1/\varepsilon_0)(\partial P_\gamma / \partial E),
\]

at each electric field therefore, the following equation is adopted to analyze the field dependence of dielectric constant:

\[
\varepsilon(E) = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4 + \left[\frac{P_r L^3}{\varepsilon_0}\right][\cosh(E \chi)]^{-2}
\]

(5.4)

where $\chi = \frac{P_r L^3}{2k_BT}$ with the cluster polarization $P$ and diameters $L$, $\varepsilon_{1,2,3}$ and $\varepsilon_0$ designate the linear, nonlinear, and high-order dielectric constant and that of vacuum, respectively. The Langevin-type term of the right side in Eq. (5.4) describes the contribution from the possible polar clusters. The other terms of the right side of Eq. (5.4) describes background dielectric response, which might correspond to the electric-field dependence of $\varepsilon$ of the host lattice.

Eq. (5.4) was used to fit the electric field dependent K data at temperatures of 60°C, 40°C, 20°C, and 0°C. It can be seen from Fig. 5-4 that the fitting curves (solid lines) are in good agreement with the experimental data. The obtained parameters $\varepsilon_1, \varepsilon_2$ and $\varepsilon_3$ as a function of temperature are shown in Fig. 5-5. The size and polarization of the polar cluster obtained by fitting are shown in Fig. 5-6. The analysis shows that the size of polar cluster grows with decreasing temperature whereas the carried polarization is smaller with decreasing temperature. All parameters obtained from fitting curves are concluded in Table 5-1.
Figure 5-4: Bias field dependence of $K$ for Nb$_2$O$_5$(0.95):TiO$_2$(0.05) single crystal at 60, 40, 20 and 0°C. The symbols: experimental data; the solid curves: the fit to Eq. 5.4.
Figure 5-5: Temperature dependence of the linear dielectric constant $\varepsilon_1$ and the nonlinear terms $\varepsilon_2$ and $\varepsilon_3$ obtained by the best fits of the dc electric field dependence of $\varepsilon$ to Eq. 5.4.
Figure 5-6: Temperature dependence of the polar cluster polarization ($P$) and size ($L$) obtained by the best fits of the dc electric field dependence of $\varepsilon$ to Eq. 5.4.
Table 5-1: Fitted parameter obtained from modified Devonshire relation

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_2$ (m²/V²)</th>
<th>$\varepsilon_3$ (m⁴/V⁴)</th>
<th>P (C/m²)</th>
<th>L (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>423</td>
<td>$3.72 \times 10^{-11}$</td>
<td>$3.62 \times 10^{-24}$</td>
<td>0.0018</td>
<td>21.5</td>
</tr>
<tr>
<td>40</td>
<td>404.89</td>
<td>$2.82 \times 10^{-11}$</td>
<td>$2.92 \times 10^{-24}$</td>
<td>0.0016</td>
<td>25.2</td>
</tr>
<tr>
<td>20</td>
<td>387.98</td>
<td>$2.58 \times 10^{-11}$</td>
<td>$3.01 \times 10^{-24}$</td>
<td>0.0005</td>
<td>31.5</td>
</tr>
<tr>
<td>0</td>
<td>339.22</td>
<td>$2.25 \times 10^{-11}$</td>
<td>$1.76 \times 10^{-24}$</td>
<td>0.0003</td>
<td>35.0</td>
</tr>
</tbody>
</table>
The type of polar clusters formed in this solid solution was believed to be generated from the existence of the Magneli phases, \( \text{Nb}_2\text{O}_{5.\delta} \), which were derived from reduction of \( \text{Nb}_2\text{O}_5 \). The obtained cluster sizes (\( L = 35-21.5 \text{ nm} \)) was reasonable and in agreement with the lattice parameters of Magneli phases.

5.4 Summary

By applying dc electric field, significant suppression of \( K \) and \( \tan \delta \) is observed. The electric field dependence of the dielectric constant can be well described by modified Devonshire relation including the cluster term. The polar clusters carry polarization \( P = \sim 0.03-0.18 \mu \text{C/cm}^2 \) and the cluster size, \( L = \sim 35-21.5 \text{ nm} \) from 0°C to 60°C. This indicates that the relaxation probably results from the distributions of cluster polarizations and cluster sizes. This remark is consistent with the work of relaxor materials made by Viehland et al.\(^1\). It was shown that a small size variation can induce a dielectric dispersion covering several frequency decades. At this stage the conclusion for the exact type of polar cluster existed and their sizes in this sample cannot be reached, and the future work is needed.
5.5 References

Chapter 6

THERMAL EXPANSION PROPERTIES

Previous chapter showed that the existence of polar nanoclusters causes the unusual dielectric behaviors of these material systems. This chapter is intended to study the influence of nanoscale distribution of Magneli’s phases on the thermal expansion behavior of the samples.

Measurements of thermal expansion have greatly increased our knowledge of material properties such as lattice dynamics, electronic and magnetic interactions, thermal defects, and phase transitions. To understand the characteristics of a new solid-solution system, thermal expansion is one of the major characteristics that should be thoroughly investigated.

6.1 Introduction

6.1.1 Methods for the Measurement of the Thermal Expansion of Solid

Many different methods and variations of methods for measuring the thermal expansion of solids have been developed. Broadly speaking, all methods for measuring thermal expansion may be divided into two classes: (1) relative methods in which the expansion of the material being investigated is measured relative to the expansion of another material; and (2) absolute methods in which the expansion of material being
investigated is measured directly. The method that is available here is called the push-rod dilatometer method. Basically two systems of dilatometers are offered; (1) single rod dilatometry and (2) dual rod (differential) dilatometry. The latter was used to measure the thermal expansion behavior of samples.

Differential dilatometry is based on a simple principle; by measuring the difference in expansion between a specimen and an accurately known standard material, high accuracy, resolution and visibility of expansion anomalies are obtained. Thermal and physical symmetry of the measuring apparatus make measuring system compensation essentially unnecessary. To maintain this symmetry and gain the most from differential technique, the specimen and standard should be of nearly the same length, and should have similar coefficients of expansion.

6.1.2 Coefficient of Thermal Expansion

The coefficient of linear expansion is the change in length resulting from a temperature change of one degree. Three different expressions are used to express the linear expansion

6.1.2.1 Coefficient of linear thermal expansion

Linear thermal expansion is symbolically represented by $\frac{\Delta L}{L_0}$ of test specimen,
where $\Delta L$ is the observed change in length $\Delta L = L_2 - L_1$, and $L_0$, $L_1$, and $L_2$ are the lengths of the specimen at reference temperature $T_0$ and test temperature $T_1$ and $T_2$. Linear thermal expansion is often expressed as a percentage or in part per million.

$$\frac{\Delta L}{L_0} = \frac{(\Delta L)_a}{L_0} + \frac{(\Delta L)_s}{L_0} \quad (6.1)$$

where: $(\Delta L)_a$ is the apparent change in specimen length

$(\Delta L)_s$ is the change in length of the dilatometer measuring system.

### 6.1.2.2 Mean coefficient of linear thermal expansion

The mean coefficient of linear thermal expansion $\bar{\alpha}$ is the average coefficient from the temperature range of $T_1$ to $T_2$. $\bar{\alpha}$ is therefore obtained by dividing the linear expansion $\frac{\Delta L}{L_0}$ by the temperature $\Delta T$. Normally $\bar{\alpha}$ is expressed in part per million per degree Centigrade.

$$\bar{\alpha} = \frac{\Delta L}{L_0} \times \frac{1}{T_2 - T_1} \quad (6.2)$$
6.1.2.3 Instantaneous coefficient of linear thermal expansion

The instantaneous coefficient of linear thermal expansion $\alpha_i$ is the expansion coefficient at any temperature $T$. Actually $\frac{\Delta L}{\Delta T}$ is the slope of the observed change in length versus the temperature curve at temperature $T$.

$$\alpha_i = \frac{1}{L_0} \frac{dL}{dT} \quad (6.3)$$

The value of the instantaneous coefficient must be accompanied by the temperature at which it is determined.

6.1.3 Literature Review of Thermal Expansion of Nb$_2$O$_5$

A large volume of literature is available on the polymorphism of Nb$_2$O$_5$, and the existence of no less than 15 polymorphs have been reported. In 1941, Brauer reported that Nb$_2$O$_5$ exist in three crystalline modifications and exhibit the following transformations: amorphous to $\gamma$ at 500°C, $\gamma$ to $\beta$ at 1000°C, and $\beta$ to $\alpha$ at 1100°C. In 1951, Hahn published X-ray data for an unspecified form of Nb$_2$O$_5$. The pattern did not correspond to Brauer’s $\alpha$, $\beta$, or $\gamma$ forms. Subsequently, Schafer et al. presented the results of a partial X-ray investigation of the Nb$_2$O$_5$ –Ta$_2$O$_5$ system that included a study of the polymorphism of Nb$_2$O$_5$. This work confirmed the $\alpha$, $\beta$, and $\gamma$ polymorphs reported by Brauer. However, the transformation temperatures differed significantly. As Schaefer
et al. pointed out, it is generally agreed that all varieties transform rapidly at temperatures above 1100°C to monoclinic H-Nb$_2$O$_5$, the high-temperature form. Several workers$^{1,2,7}$ have independently verified that the transformation is irreversible and that the monoclinic form is the truly stable form.

Manning et al.$^8$ reported the lattice parameters of monoclinic H-Nb$_2$O$_5$ as a function of temperature from room temperature to 1350°C, revealing that its lattice thermal expansion is anisotropic. Past work$^{8-12}$ has revealed the low thermal expansion behavior of Nb$_2$O$_5$. Durbin and Harman$^9$ were probably the first to report the low expansion of Nb$_2$O$_5$ as measured by dilatometer; data were obtained on heating only. They found that the average coefficient of thermal expansion was 0.48 x 10$^{-6}$ °C$^{-1}$ from 25 to 900°C. Douglass$^{10}$ used a dilatometer to measure the linear thermal expansion of stoichiometric and nonstoichiometric hot-pressed Nb$_2$O$_5$. The differences between the values for the stoichiometric and nonstoichiometric oxides were small; slightly higher values were observed for the latter. The average expansion coefficient from 20 to 900°C, calculated from the data of Douglass, is 1.59 x 10$^{-6}$ °C$^{-1}$, a value roughly three times that reported by Durbin and Harman. Manning et al. reported the bulk linear thermal expansion of both sintered and hot-pressed samples of Nb$_2$O$_5$, as determined with a dilatometer from room temperature to 1200°C. The overall linear expansion of the least porous sintered sample was unusually small, and hysteresis was observed between heating and cooling data. Most recently, Ota et al.$^{13}$ described the thermal expansion of polycrystalline H-Nb$_2$O$_5$ ceramics and their Magneli phase, Nb$_2$O$_{5-x}$. The average thermal expansion of the H-Nb$_2$O$_5$ unit cell was relatively low, and the thermal expansion of the
H-Nb₂O₅ ceramic was even lower, because microcracks developed by the crystallographic anisotropy present during thermal expansion. All members of the nonstoichiometric Nb₂O₅₋ₓ series of ceramics also showed low thermal expansion. A Magneli phase showed abrupt expansion after it was oxidized because of the transition to metastable Nb₂O₅.

6.1.4 Negative Thermal Expansion Materials from the Literatures

It is well known that the vast majority of materials have a positive coefficient of thermal expansion; that is, they expand on heating, a property which can have deleterious effects in eventual applications. The possibility of designing and manufacturing materials with a negative coefficient of thermal expansion that is a class of materials which contract on heating, is clearly of interest [Roy et al., 1989].

Negative thermal expansion (NTE) materials have received considerable attention during the last decade. They have a number of important potential uses in ceramic, optical, and electronic applications. Such materials either as pure phases or as constituents of composite materials designed to achieve a desired overall coefficient, which can include zero thermal expansion. Ranges of applications are including zero-expansion heat sink, printed circuit boards, dental applications, substrates for high-precision optical applications, low temperature thermocouples and thermal switches, catalyst supports, and cookware etc.

Matching the thermal expansion of device parts can be important to avoid cracks or separation at interfaces between two components, and zero expansion is needed when
exact positioning of electronic or optical components in a device is crucial. It has recently been demonstrated that the use of a composite containing the NTE material cubic ZrW$_2$O$_8$ can prevent the expansion of optical fiber gratings [Flemming et al., 1997].

Prior to the recent interest in NTE materials, several families of compounds had been investigated because of their low expansion coefficients. Prominent examples are lithium aluminum silicates (LAS) [Hummel, 1951] and the NaZr$_2$P$_3$O$_{12}$ (NZP) family [Boilot et al., 1979 and Limaye et al., 1991]. Materials based on LAS and NZP ceramics or glasses have found a wide variety of uses. However, some applications require NTE (e.g. temperature compensation of optical fiber), and others demand zero thermal expansion along with another property (e.g. insulator, conductor, strength, flexibility etc.) that may not be intrinsic to the low expansion material. This makes the use of NTE materials as fillers in composites attractive, as they can counterbalance the normal positive expansion of the matrix material while the matrix provides some valuable property. The recent work on Cu/ZrW$_2$O$_8$ composites is an example of this approach.

An ideal NTE material should undergo isotropic and preferably linear negative expansion over a large temperature range including room temperature. It should also be accessible from cheap, commercially available precursors and easy to prepare. For use in composites, it is desirable that the material is thermodynamically stable over a large temperature and pressure range. The material should not undergo phase transitions at low pressures, as the composite matrix may compress the filler during processing and use. In reality, no known material fulfills all of these requirements.

Recently, the interest in negative thermal expansion materials and their potential applications is growing and several new materials have been identified. The numerous
studies of ZrW₂O₈ have been investigated as it shows a large isotropic negative thermal expansion over a wide range of temperature (0-1050 K). The coefficient of this thermal contraction (\( \alpha = -8.8 \times 10^{-6} \text{ K}^{-1} \)) is of the same order of magnitude as that of a high expansion normal ceramic such as Al₂O₃ (\( \alpha = 9 \times 10^{-6} \text{ K}^{-1} \)). Unfortunately, there are some drawbacks to this material. ZrW₂O₈ is only thermodynamically stable at high temperatures. The expansion curve shows a discontinuity around 430 K, where the material undergoes a cubic-to-cubic phase transition (\( \alpha \) to \( \beta \)). This changes the linear expansion coefficient from -8.8 to -4.9 \( \times 10^{-6} \text{ K}^{-1} \). Lind et al. (1998) had synthesized ZrMo₂O₈ to improve the properties of NTE material. Cubic ZrMo₂O₈ is isostructural with \( \beta \)-ZrW₂O₈ and display NTE with \( \alpha = -5.0 \times 10^{-6} \text{ K}^{-1} \) between -262 and 300°C. No phase transitions are observed in this temperature range. The unusual negative thermal expansion is also discovered in a large family of molybdates and tungstates of the type \( A_2(MO_4)_3 \), where \( A \) is an octahedral cation and \( M \) is Mo⁶⁺ or W⁶⁺ such as Sc₂W₃O₁₂ and Lu₂W₃O₁₂. A number of compounds that give the negative thermal expansion is listed in Table 6-1.
Table 6-I: Negative thermal expansion coefficient materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Structure</th>
<th>$\alpha \times 10^{-6}$ °C$^{-1}$</th>
<th>Temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>Faujasite structure</td>
<td>-4.2</td>
<td>25-573 K</td>
</tr>
<tr>
<td>Sc(WO$_4$)$_3$</td>
<td>Cubic</td>
<td>-6 - -11</td>
<td>0-800°C</td>
</tr>
<tr>
<td>ZrW$_2$O$_8$</td>
<td>Cubic</td>
<td>-8.8</td>
<td>0.3-1050 K</td>
</tr>
<tr>
<td>Lu$_2$W$<em>3$O$</em>{12}$</td>
<td>Cubic</td>
<td>-6.8</td>
<td>127-627°C</td>
</tr>
<tr>
<td>ZrMo$_2$O$_8$</td>
<td>Cubic</td>
<td>-5</td>
<td>-262 - +300°C</td>
</tr>
<tr>
<td>NbOPO$_4$</td>
<td>Orthorhombic</td>
<td>-3.6</td>
<td>400-700°C</td>
</tr>
<tr>
<td>AlPO$_4$</td>
<td>Hexagonal erionite</td>
<td>-11.7</td>
<td>18-300 K</td>
</tr>
</tbody>
</table>
6.1.5 Mechanism of Negative Thermal Expansion

Four important mechanisms for intrinsic thermal expansion in oxides have been identified. One mechanism pertains to ferroelectric oxides. Negative thermal expansion exists in BaTiO$_3$, PbTiO$_3$, and some other AMO$_3$ oxides with the perovskite structure just below their cubic-to-tetragonal phase transitions. In the low temperature, tetragonal region the TiO$_6$ and AO$_{12}$ polyhedra become more regular with increasing temperature. It is well known that the average metal-oxygen (M-O) distances in polyhedra decrease as the polyhedra become more regular.\textsuperscript{35} This effect can be attributed to the fact that anion-anion repulsions are minimized as polyhedra become more regular. This effect is found in PbTiO$_3$ because both the PbO$_{12}$ and TiO$_6$ polyhedra change significantly as the temperature changes in the tetragonal structure. In the low-temperature, tetragonal range, there is thermal expansion along the $a$ and $b$ axes, and thermal contraction along the $c$ axis. This results in a small unit cell volume thermal contraction in the tetragonal structure. Once PbTiO$_3$ becomes cubic, they show normal positive thermal expansion.

A second mechanism is actually caused by the normal positive thermal expansion of certain M-O bonds.\textsuperscript{36} Example of this mechanism is found in NZP (NaZr$_2$P$_3$O$_{12}$) which has hexagonal structure and shows highly anisotropic thermal expansion. In NZP, thermal expansion occurs along the $c$ axis with thermal contraction along $a$ and $b$ axes. The net effect is a very low volume thermal expansion. The strong P-O and Zr-O bonds show negligible thermal expansion in this structure, whereas significant thermal expansion occurs for the weaker Na-O bond.\textsuperscript{37} In NZP, chains of face-shared octahedral expand along the $c$ axis on being heated. These chains are pulled together by twisting P-O
bonds which do not change length. Thus, there is a thermal contraction along the \( a \) and \( b \) axes. This second mechanism can rationalize negative thermal expansion in one or two dimensions.

The third mechanism for negative thermal expansion is based on interstitial cation within a network changing sites as a function of temperature. This factor becomes important for \( \beta \)-eucryptite and the NZP family where ionic conductivity is significant. In \( \beta \)-eucryptite, the \( \text{Li}^+ \) cations are predominantly on tetrahedral sites. Some movements of \( \text{Li}^+ \) to octahedral sites cause the observed negative volume thermal expansion.

A fourth mechanism is based on the transverse thermal motion of oxygen in M-O-M linkages.\(^{16}\) If one considers a simple M-O-M bond (Fig. 5-1), the shape of a typical M-O potential implies that longitudinal oxygen vibrations will in general cause an increase in M-O and, consequently, M-M distances. A transverse vibration in which individual M-O bond distance are unchanged, however, can lead to a reduction in M-M distance; the greater the mean square displacement of the O atom the greater the effective reduction in M-M distance.
Figure 6-1: A schematic representation of how transverse thermal vibrations of M-O-M bonds can give rise to NTE in framework oxide structures. [After Evan et al. (1998)]
Generalizing to two and three dimensions (Fig. 6-1), in a framework inorganic structure transverse vibrations of individual M-O-M linkages can occur in a cooperative manner such that one can consider the vibrations of essentially undistorted MO\textsubscript{n} coordination polyhedra. These polyhedra liberation can give rise to negative thermal expansion.

The requirements for a compound to show low or negative thermal expansion can be summarized as:

(i) The presence of strong M-O bonds which themselves have inherently low expansion; high M-O covalency; e.g. \( M = W^{6+}, Nb^{5+}, Si^{4+} \).

(ii) 2 coordinate oxygen to allow transverse vibrations

(iii) Framework structure with topology to support low-energy transverse vibrational modes.

(iv) No interstitial framework cations.

(v) Absence or suppression of displacive phase transitions to lower symmetry, lower volume structures.

6.2 Experimental Procedure

6.2.1 Sample Preparation

The specimens with length 3-6 mm were prepared by dicing and polishing. They were subjected to thermal annealing at 700°C for 3 hours to eliminate stresses induced during polishing.
6.2.2 Instrument and Procedure

Thermal expansion measurements were carried out from -150°C to 600°C by using a horizontal push-rod dilatometer (DilatronicTM, Theta Industries, NY) equipped with a highly sensitive linear variable differential transformer (LVDT). LVDT is a sensitive electromechanical transducer that produces an electrical output proportional to the displacement of a separate core. Fused silica rods were used as reference expansion (~5 x 10^-7/°C over the useful temperature range). Any expansion in the fused silica was presumably compensated for as the specimen was placed in between the same material. Heating and cooling rates were maintained at 2°C/min allowing sufficient time for the thermal fluctuations to stabilize at each step. Liquid N₂ cooling and electrical heating was used to vary the chamber temperature.

Single-crystal rods cut with length parallel to either the c or a axis were mounted inside a fused silica holder that is set upright in a vertical furnace, and the thermal expansion or contraction were recorded on an X-Y recorder. When the thermal-expansion-vs.-temperature curves showed hysteresis behavior between the heating and cooling, each measurement was performed at least two more times to make certain that the hysteresis behavior was the same for each sample.
6.3 Negative Thermal Expansion Behavior in Single Crystal and Ceramic of Nb$_2$O$_5$-Based Compositions

6.3.1 Thermal Expansion of Pure Nb$_2$O$_5$ Single Crystal

A single crystal of Nb$_2$O$_5$ was grown by the LHPG technique. The growth temperature was 1500°C and the speed ratio of seed/feed was 20/20 mm/h. Because the ceramic was used as seed, the precise growth orientation was not determined. The thermal expansions of a single crystal cut perpendicular to the growth direction or a single crystal cut parallel to the growth direction were measured in the range of –150-500°C. Figures 6-2 and 6-3 show the thermal expansion curves of an Nb$_2$O$_5$ single crystal cut perpendicular to the growth direction. The curve in Fig. 6-2 exhibits a negative slope, which implies contraction. During the first heating cycle, the abrupt thermal expansion occurred at 200°C and a shift to higher temperature in the cooling cycle. According to past work, an abrupt thermal expansion was found in the Magneli phase (Nb$_2$O$_{5-x}$) as a result of the transition between metastable Nb$_2$O$_5$ phases oxidized stepwise in air. Figure 6-3 has been plotted to show the thermal coefficient ($\alpha$) of the Nb$_2$O$_5$ single crystal in the first heating run. The average coefficient of an Nb$_2$O$_5$ single crystal before reaching 200°C is $-2 \times 10^{-6}$ °C$^{-1}$, after 300°C, it is $-4 \times 10^{-6}$ °C$^{-1}$. These coefficients are quite large when compared with the previous reports. Figure 6-4 shows the full cycle of thermal expansion measurements of the side of an Nb$_2$O$_5$ single crystal (same specimen as Fig. 6-2). The curves still exhibit a negative slope. The abrupt thermal expansion has disappeared because of the difference in heat treatment. Hysteresis between heating and cooling data is quite evident. In the case of the single-phase polycrystalline ceramic,
several workers have attributed thermal expansion hysteresis to the occurrence and healing of internal microcracks caused by thermal-expansion anisotropy. In the case of a single crystal, microcracks are easily produced in the crystals during growth because the temperature gradient in the molten zone is large; this might be the cause of the hysteresis.
Figure 6-2: Full measurement cycle of thermal expansion of Nb$_2$O$_5$ single crystal fiber (cross section), showing contraction of single crystal and an abrupt change of thermal expansion in first heating run.
Figure 6-3: Thermal expansion of Nb$_2$O$_5$ single crystal fiber (first heating run) showing negative thermal expansion coefficient and a sharp phase transition at temperature 250°C.
Figure 6-4: Full measurement cycle of thermal expansion of Nb$_2$O$_5$ single crystal fiber (parallel plane); same specimen as of Fig. 6-2.
6.3.2 Thermal Expansion of Nb$_2$O$_5$-TiO$_2$ Ceramics and Single Crystals

Powder XRD patterns were first collected for Nb$_2$O$_5$(1-x): TiO$_2$(x) (x = 0.05, 0.08, 0.11) polycrystalline ceramics and single crystals. All indexing corresponds to the monoclinic H-Nb$_2$O$_5$ structure, which is quite reasonable inasmuch as our single crystals are grown at high temperature (≈1500°C) and under steep temperature-gradient conditions. Therefore, the H-Nb$_2$O$_5$ phase is the most probable phase in the grown fibers. The thermal expansion curves of all three compositions were negative and accompanied by hysteresis, as seen in Fig. 6-5. Nb$_2$O$_5$(0.95): TiO$_2$(0.05) (Fig. 6-5(a)) shows the largest hysteresis area. The hysteresis does not close because the new crack system is different from that present at the beginning of the run. The change in the crack system also explains why repeated thermal expansion runs on the same specimen are not identical. Rather than being generated by internal microcracks, as in the sintered ceramic, hysteresis can occur when the expansion coefficients of the mixture differ. The thermal expansion coefficient of TiO$_2$ is 6.8 x 10^{-6} °C^{-1}, whereas that of Nb$_2$O$_5$, in general, is < -2 x 10^{-6} °C^{-1}. Figure 6-6(a) shows the full measurement cycle of thermal expansion of an Nb$_2$O$_5$(0.89):TiO$_2$(0.11) single crystal. Again, the negative thermal expansion and hysteresis are observed. The cooling-run data were separated in Fig. 6-6(b) to emphasize the phase transition at 150°C. This phase transition was also discovered in the dielectric measurement of the same specimen; the data under the cooling run are recorded, in Fig. 6-7. In general, this work shows that the thermal expansion coefficients of single crystals are much more negative than those of polycrystalline ceramics.
Figure 6-5: Thermal expansion of Nb₂O₅(1-x):TiO₂(x) ceramics.
Figure 6-6: (a) Full measurement cycle of thermal expansion of Nb$_2$O$_5$(0.89):TiO$_2$(0.11) single crystal, showing contraction of single crystal. (b) First cooling run, showing phase transition at 150°C.
Figure 6-7: Temperature dependence of dielectric constant (K) of Nb$_2$O$_5$(0.89):TiO$_2$(0.11) single crystal, showing phase transition at the same range of temperature.
6.4 Thermal Expansion of Nb$_2$O$_5$-SiO$_2$ Ceramics and Single crystal

Figure 6-8 shows the full measurement cycle of thermal expansion of Nb$_2$O$_5$(1-x):SiO$_2$(x) ceramics. For Nb$_2$O$_5$(0.95):SiO$_2$(0.05) ceramic, the result shows three temperature regions of different thermal expansion coefficients ($\alpha$); (1) -150°C to 30°C, $\alpha = -0.6 \times 10^{-6}$ °C$^{-1}$, (2) 30°C to 260°C, $\alpha = 0.1 \times 10^{-6}$ °C$^{-1}$, (3) 260°C to 550°C, $\alpha = 0.5 \times 10^{-6}$ °C$^{-1}$. As Si content is increased to 11 mole %, the Nb$_2$O$_5$(0.89):SiO$_2$(0.11) gave the higher positive thermal expansion coefficient in regions 2 and 3 but less negative thermal expansion coefficient in region 1, as follows; (1) -150°C to 30°C, $\alpha = -0.5 \times 10^{-6}$ °C$^{-1}$, (2) 30°C to 260°C, $\alpha = 0.3 \times 10^{-6}$ °C$^{-1}$, (3) 260°C to 550°C, $\alpha = 0.9 \times 10^{-6}$ °C$^{-1}$. These results of thermal expansion coefficients are reasonable because the thermal expansion coefficients of both end members have nearly similar value but opposite sign. Nb$_2$O$_5$ has the thermal expansion coefficient of $-2 \times 10^{-6}$ °C$^{-1}$ and SiO$_2$ has the thermal expansion coefficient of $3 \times 10^{-6}$ °C$^{-1}$. These results show the potential to make the compound with zero thermal expansion coefficient for various applications.

However, the thermal expansion coefficient of these solid solutions in single crystal form shows the negative thermal expansion throughout the measurement temperature range. The negative thermal expansion coefficient of Nb$_2$O$_5$(0.95):SiO$_2$(0.05) single crystal is valued $-3.1 \times 10^{-6}$ °C$^{-1}$. 
Figure 6-8: Thermal expansion of Nb$_2$O$_5$(1-x):SiO$_2$(x) ceramics.
Figure 6-9: Thermal expansion of Nb$_2$O$_5$(0.95):SiO$_2$(0.05) single crystal, showing negative thermal expansion throughout the measurement temperature range.
6.5 Thermal Expansion of Nb$_2$O$_5$-Al$_2$O$_3$ Ceramics and Single crystal

Al$_2$O$_3$ is well known to have high thermal expansion coefficient, $\sim 8.8 \times 10^{-6}$ °C$^{-1}$. When making the solid solution with negative thermal expansion coefficient materials, the thermal expansion coefficient of solid solution should be decreased. Figure 6-10 shows the full measurement cycle of thermal expansion of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) ceramics. At low temperature (-150°C to 30°C), all three ceramics exhibit the negative thermal expansion behaviors whereas the high temperature region shows the positive thermal expansion coefficient. However, the temperature region of negative thermal expansion was narrower as the content of Al$_2$O$_3$ was increased. Nb$_2$O$_5$(0.95):Al$_2$O$_3$(0.05) ceramic shows the value of $\alpha_{-150-25^\circ C} = -1.25 \times 10^{-6}$ °C$^{-1}$, $\alpha_{25-350^\circ C} = 0.1 \times 10^{-6}$ °C$^{-1}$, and $\alpha_{350-550^\circ C} = 0.5 \times 10^{-6}$ °C$^{-1}$. Nb$_2$O$_5$(0.92):Al$_2$O$_3$(0.08) ceramic shows the value of $\alpha_{-150-0^\circ C} = -1.1 \times 10^{-6}$ °C$^{-1}$, $\alpha_{0-300^\circ C} = 0.2 \times 10^{-6}$ °C$^{-1}$, and $\alpha_{300-550^\circ C} = 0.75 \times 10^{-6}$ °C$^{-1}$. Nb$_2$O$_5$(0.89):Al$_2$O$_3$(0.11) ceramic shows the value of $\alpha_{-150-0^\circ C} = -1.1 \times 10^{-6}$ °C$^{-1}$, $\alpha_{0-300^\circ C} = 0.6 \times 10^{-6}$ °C$^{-1}$, and $\alpha_{300-550^\circ C} = 1.2 \times 10^{-6}$ °C$^{-1}$.

Figure 6-11 exhibits the thermal expansion of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) single crystals. The negative thermal expansion behavior was observed as same as those of Nb$_2$O$_5$(1-x):TiO$_2$(x) single crystals and Nb$_2$O$_5$(1-x):SiO$_2$(x) single crystals. The thermal expansion of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) single crystals shows negative thermal expansion coefficient with the average value of $-1.6 \times 10^{-6}$ °C$^{-1}$. 
Figure 6-10: Thermal expansion of Nb_2O_5(1-x):Al_2O_3(x) ceramics; the arrow indicates the starting point of measurement.
Figure 6-11: Thermal expansion of Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) single crystal, showing negative thermal expansion throughout the measurement temperature range.
6.6 Thermal Treatment History Effect

6.6.1 Thermal Expansion of Sample with Different Sintering Conditions

To investigate the relationship of the thermal expansion with the processing history, Nb$_2$O$_5$(0.89):SiO$_2$(0.11) ceramic was prepared under five different sintering conditions (1350°C/3h, 1400°C/24h, 1400°C/48h, 1400°C/72h, and 1400°C/96h respectively). The ceramic sample was first sintered at 1350°C for 3 hours and was measured the thermal expansion before it was sintered again in following conditions. This is the same sample that was used to investigate the sintering effect to the dielectric properties of ceramic. The thermal expansion measurement starts from room temperature and then cooling to -150°C before heating to 600°C. The measurement loop was taken two times to make sure the expansion is certain.

Figure 6-12 shows the results of thermal expansion of sample at different sintering history. First sintering, 1350°C/3h, the sample suggested the average of positive thermal expansion coefficient throughout the temperature range of -150 to 600°C. When sintered again at 1400°C/24h, the positive thermal expansion coefficient was dramatically decreased and the negative thermal expansion coefficient was observed at low temperature range, ~-150 to 0°C. As the sintering time was prolonged, the temperature region of negative thermal expansion coefficient was broader to high temperature region. As the sample was sintered at 1400°C/96h, the negative thermal expansion was obtained from -150°C to 250°C.
6.6.2 Structure-Property Relationships

To explain the thermal expansion behavior of a ceramic with different sintering history, the density of the ceramic at each sintering stage was measured and the microstructure was observed by SEM technique.

6.6.2.1 Density Measurement

The density increased with sintering temperature or sintering time, as concluded in Table 4-7.

6.6.2.2 Microstructure by Scanning Electron Microscopy

The SEM micrographs of sintered surface of sample at each sintering stage can be viewed from Figure 4-33. For the sample sintered at 1350°C/3h, the grain size was small with intragranular porosity. It looks like the ceramic at this sintering stage was not fully sintered. When the sample was heated in thermal expansion measurement, the grain was continually grown in porous space and gave the positive thermal expansion coefficient. The pores in ceramic could cause the hysteresis in thermal expansion loop. Higher sintering temperature enables grain growth and reductions of porosity. Longer sintering time, the elongated grains were developed, about 10 µm in sample sintered at 1400°C/48h then increasing to 20 µm in sample sintered at 1400°C/96h. The grain structure becomes anisotropic, although the density was improved.
Figure 6-12: Thermal expansion of Nb₂O₅(0.89):SiO₂(0.11) ceramics sintered at different conditions.
6.7 Summary

The bulk linear thermal expansion of sintered ceramics and single crystals of 
Nb$_2$O$_5$-based composition was determined with a dilatometer in the temperature range of 
$-200$-$600^\circ$ C. The overall linear expansion of all specimens was negative in both parallel 
and perpendicular direction to the growth of the samples, and hysteresis was observed 
between heating and cooling data. The occurrence and recombination of internal 
microcracks caused by thermal expansion anisotropy apparently contribute to the 
hysteresis and to the difference in thermal expansion coefficient of the mixtures. 
Differing heat treatment causes changes in thermal expansion behavior. The thermal 
expansion coefficients of single crystals are much more negative than those of sintered 
ceramics. The phase transition in a single crystal of the Nb$_2$O$_5$-TiO$_2$ system, as observed 
by dielectric measurement, can be verified by thermal expansion data.

The associated origin of the negative expansion has not been investigated in this 
thesis but it could be highly probable that Magneli’s phases are playing a role in a 
composite structure. Materials exhibiting negative thermal expansion through room 
temperature have a variety of applications, mainly in controlling the overall thermal 
expansion of various composites.

Nevertheless, the thermal expansion coefficient of these solid solutions in ceramic 
form can be designed to achieve a desired overall coefficient by either annealing or 
processing history.
6.8 References


Chapter 7
CONCLUSIONS AND FUTURE WORK

In addition to the specific sets of conclusions presented in the previous chapters, several general conclusions can be drawn from the work and are summarized in this chapter.

7.1 Conclusions

The ceramics of solid-solution Nb$_2$O$_5$(1-x):TiO$_2$(x), Nb$_2$O$_5$(1-x):SiO$_2$(x), and Nb$_2$O$_5$(1-x):Al$_2$O$_3$(x) for x = 0.05, 0.08, 0.11 were fabricated by using the conventional solid state reaction.

The single crystals of these solid-solutions were grown successfully by the Laser-Heated Pedestal Growth technique which was designed and assembled here at the Materials Research Laboratory. The grown single crystal fibers were characterized for crystal structure composition evaluation and for anisotropic property measurements.

The dielectric measurements of Nb$_2$O$_5$-based oxides ceramics and single crystals revealed important characteristics of this system and the results on the Nb$_2$O$_5$ system are classified in three specific areas:

1) The unusual enhancement of dielectric constant of Nb$_2$O$_5$ has been observed through the small substituents such as TiO$_2$, SiO$_2$, and Al$_2$O$_3$. 
1a) The dielectric properties of Nb$_2$O$_5$ were extremely sensitive to the small substitutions of the selected oxides. By varying the content of additive TiO$_2$, the dielectric constant of Nb$_2$O$_5$(1-x):TiO$_2$(x) ceramics were increased by increasing the amount of TiO$_2$. A low concentration of TiO$_2$ dopant (0.05-0.11 mole %) evidently suppressed the conductivity (which perhaps is associated with the multiple valence of Nb$^{5+}$ ion) behavior of pure Nb$_2$O$_5$.

1b) Small substitutions of SiO$_2$ and Al$_2$O$_3$ were also found to enhance the dielectric properties of Nb$_2$O$_5$ as well. The difference is by increasing the contents of SiO$_2$ and Al$_2$O$_3$, the dielectric constant of solid solution ceramics was decreased. The maximum of dielectric constants were observed in ceramic compositions, Nb$_2$O$_5$(0.95):SiO$_2$(0.05) and Nb$_2$O$_5$(0.95):Al$_2$O$_3$(0.05) in their respective systems.

2) This work is the first report on the single crystal growth of the solid solution and the anisotropic dielectric behavior of the crystals.

2a) Single crystals of various solid solution compositions were grown successfully. The current dielectric properties study is the first reported work on the single crystals of these systems. Single crystals were characterized by X-ray and confirmed to be of high temperature H-Nb$_2$O$_5$ phase. In single crystal forms, the high anisotropic dielectric properties were observed. The dielectric properties dependant on the crystal orientation. High dielectric constant (on the order of 1000) was found in the perpendicular plane to the growth direction whereas low dielectric constant (on the order of 10 or 100)
was found in the parallel plane to the growth direction. No specific attempts were made to precisely orient the crystal planes for such measurements.

2b) The frequency dependence of dielectric constant or dielectric dispersion was found to be a major common characteristic of Nb$_2$O$_5$ based oxide solid solution systems selected for the current studies. The relaxation parameters were analyzed using the approaches such as Debye, Arrhenius, Cole-Cole, and Vogel-Fulcher relationships. The analysis was indicative of ionic jump or dipole relaxations as associated mechanism at low temperatures.

2c) The dielectric loss clearly was affected by the treatment of the samples in an oxidizing atmosphere, which suggests that the oxygen-vacancy concentration is closely responsible to the dielectric relaxation and supports the previous analysis, indicating an oxygen-ion-jump loss mechanism.

2d) The oxygen vacancy (or multiple Nb ion valences) causes the occurrence of the Magneli’s phases in these systems. These phases are of polar monoclinic structure (point group m, 2), a hypothesis put forward that these materials may exist as polar clusters in these materials.

2e) By using the modified Devonshire relation, the cluster polarizations and cluster sizes were calculated. The cluster size distribution with temperature was observed. This could lead to the relaxation mechanism which occurs at high temperature mode.

2f) The Magneli’s phases (Nb$_2$O$_{5.8}$) were suggested to be the polar cluster types. The exact phases could not be determined at this time. However, the
calculated polar cluster sizes were corresponding to 5-10 times the lattice sizes (typically ~3-4 nm) of Magneli’s phases.

2g) The phase transitions suggested by the dielectric anomalies were supported further by the thermal expansion measurements.

3) The nanoscale distribution of Magneli’s phases also influences the thermal expansion behavior of the samples.

3a) Due to the presence of the unavoidable Magneli’s phases in these systems, unusual thermal expansion behavior from these materials is expected. In order to evaluate the potential uses of these compositions in thin film devices, the thermal expansion properties were measured by dilatometer technique in the temperature range of –200-600°C. Most of the compositions gave the negative thermal expansion over a wide temperature range of the current measurement.

3b) The overall linear expansion of all single crystals was negative in both parallel and perpendicular direction to the growth of the samples. The associated origin of the negative expansion has not been investigated in this thesis but it could be highly probable that Magneli’s phases are playing a role in a composite structure. Hysteresis was observed between the heating and cooling data. The occurrence and recombination of internal microcracks caused by the thermal expansion anisotropy thermal stresses between the phases apparently contribute to the hysteresis and to the difference in thermal expansion coefficient of the mixtures. The values of negative thermal expansion
coefficients of single crystals were much higher than those of the sintered ceramics.

By understanding the dielectric nature of these solid-solutions, the potential uses in electronic applications could be drawn and the improvements could be designed to adjust the properties to meet the requirement of each specific application.

Materials exhibiting negative thermal expansion through room temperature have a variety of applications, mainly in controlling the overall thermal expansion of various composites, designing low temperature thermal switches, etc.

Nevertheless, the thermal expansion coefficient of these solid solutions in ceramic form can be designed to achieve a desired overall coefficient by either annealing or processing history.

7.2 Suggestions for Future Work

Generally, the intrinsic properties of materials such as the microstructure, crystallographic phase, composition, play critical role to determine the electrical and physical properties of materials. It will be a great challenge to study these solid-solutions in other form such as in thin film which could present the different interesting facet of these materials. The various processing methods also are of interest.

In this work, the successful growth of single-crystals of Nb$_2$O$_5$ based oxides was presented. However, they should be additional efforts to further improve the quality of
single crystal or to have a better understanding about the crystal growth behavior of this class of materials.

Future work on the growth of single crystals by the LHPG technique could involve:

a) The growth of single crystals in various atmospheres such as in O₂, in order to control the reduction of Nb₂O₅ and other oxide at high temperature that occur during the growth.

b) The growth of single crystals by using different types of seed rod, such as the platinum wire, or the appropriate oriented single crystal seed.

c) Crystals should be grown with the precise orientation and piezo/pyroelectric nature of these materials should be evaluated. Our preliminary pyroelectric coefficient measurement data does suggest the polar behavior of the material. Along with the tunable characteristics of the material, there is a need to evaluate in detail the linkage of polar clusters with ferroelectric like behavior.

d) High resolution microscope studies are desirable to observe the nanoclusters and the antiphase boundaries along with the Magneli’s phases. Crystallographic parameters of various phases and the phase transition studies are also desirable to gain knowledge in which these phases are playing the role to enhance the dielectric properties of simple oxides.

e) Microwave frequency measurements of the dielectric properties and the relaxation behavior in these systems should be further studied to establish the potential of these materials in microelectronic devices.
VITA

Hathaikarn Manuspiya was born on March 23, 1973 in Thailand. After receiving her primary education in her hometown of Trang in the southern part of Thailand, she began her high school at the demonstration school of Prince of Songkla University, Pattani, where she could skip her one last year of high school because of her success in the nation-wide entrance examination to the Chulalongkorn University in Bangkok. In March 1994, she obtained her B.S. degree in Materials Science from Chulalongkorn University, before beginning her M.S. studies. In 1995, she was awarded the full scholarship from the National Petrochemical public company for her M.S. studies in Polymer Science at the Petroleum and Petrochemical College, Chulalongkorn University, where she was granted her M.S. degree in May 1997. She also was the recipient of the Thai government scholarship for studying doctorate degree abroad.

In August 1997, she joined the Intercollege Graduate Program in Materials of the Pennsylvania State University to begin her Ph.D. studies with Prof. Amar Bhalla at Material Research Institute (MRI). During her graduate studies here, she has published a dozen articles in scientific journals and proceedings. In addition, she has given more than 10 presentations at the national and international conferences. One of her research paper was selected as the Best Graduate Student Poster Presentation at the annual Meeting of the American Ceramics Society in 1999.