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PROCESSING AND CHARACTERIZATION OF LITHIUM NIOBATE WITH SECOND PHASE ADDITION

DISSERTATION

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

By

Jai S. Subramanian, B.S., M.S.

* * * * *

The Ohio State University

1995

Dissertation Committee:

P. K. Gallagher
S. A. Akbar
C. H. Drummond

Approved by

Patrick K. Gallagher
Adviser
Department of Materials Science & Eng.
To my parents
ACKNOWLEDGMENTS

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VITA

May 22, 1964 ............................................ Born - Trichy, India

1982 .................................................. BS, Physics, India

1985 .................................................. BS, Metallurgy, India

1988-1990 ................................. MS, Ceramic Engineering, The Ohio State University

1990-present ................................. Graduate Research assistant, The Ohio State University

PUBLICATIONS


FIELDS OF STUDY

Major Field: Materials Science and Engineering
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CHAPTER I

INTRODUCTION

Since the invention of the laser twenty five years ago, there has been a revolution in the methods of production, transmission and processing of optical signals [Alferness (1986)]. One of the advantages of using laser is the ability to pass information in the visible and infrared region of the spectrum [Prokhorov and Kuz'minov (1990)]. In order to fully exploit the potentials of the laser, devices that can modulate, deflect and control optical signals are required. These requirements have led to intensive research on producing crystals with small optical losses and the ability to control the characteristic of optical beams by the application of an electric field.

Materials in which the characteristics of an optical beam can be controlled by an applied voltage are called electro-optic materials. The control is achieved by changing the refractive index of the material utilizing the linear electro-optic effect. The application of an electric field causes a change in the refractive index (Δn) and the change in refractive index is given by [Abouelleil et al. (1989)]

$$\Delta n = n^3 r E / 2$$ (1.1)
where \( n \) is the refractive index, \( r \) the electro-optic coefficient and \( E \) the applied electric field. This index change (\( \Delta n \)) can cause a corresponding phase change (\( \Delta \phi \)) or an intensity change depending on the type of modulator considered.

Figure 1 shows the construction of a phase modulated (Figure 1, left) and an intensity modulated (Figure 1, right) electro-optic device [Bossi et al. (1992)]. The voltage induced refractive index change modifies the velocity and thus the phase of the output optical wave (Figure 1, left). The magnitude of the phase shift is proportional to the electro-optic coefficient, the applied voltage (\( V \)) and the interaction length (\( L \)). The intensity modulator is produced by combining two phase modulators. The output of the intensity modulator is a function of the relative phase delay between the two modulator sections and can result in maximum or minimum optical transmission. The output of the intensity modulator also called the Mach-Zehnder modulator (Figure 1, right) can thus be varied sinusoidally with the applied voltage.

The electro-optic switch, an important building block for integrated-optic devices is another example in which electro-optic materials are used to control the transmission of light. Figure 2 shows an electro-optic switch. The electro-optic switch consists of a pair of waveguides separated by a distance \( d \). The spacing between the two waveguides is so designed, that the evanescent tail of each waveguide extends into the other. This allows the light in the two waveguides to interact or couple [R. C. Alferness (1986)].
Figure 1. Typical applications of electrooptic devices [Bossi and Ade (1992)].
coupling efficiency is a function of the speed of light in the two waveguides and under phase-matched condition all the light injected into one waveguide will be coupled to the second after a characteristic interaction length. Figure 2 (bottom) shows the coupling efficiency or the switching response as a function of the applied voltage.

The most common electro-optic materials used in the construction of the above mentioned devices are the semiconductors gallium arsenide and indium phosphide and the ferroelectric insulating crystal lithium niobate. Lithium niobate (LiNbO₃) is the most widely used electro-optic crystal for a number of reasons. First, high quality single crystal lithium niobate substrates can be easily grown. Lithium niobate substrates have low optical transmission losses and a high electro-optic coefficient. This high electro-optic coefficient as can be seen from equation 1.1 translates to low control voltages and makes LiNbO₃ attractive for optical switching applications.

Major applications of lithium niobate require controlled waveguides. Waveguides are created by forming a region of higher refractive index surrounded by a region of lower refractive index. The waveguides so formed confine light by total internal reflection within the crystal. In lithium niobate waveguides this refractive index increase is achieved by diffusion of titanium into the crystal.

The various steps involved in the process of fabrication of a waveguide by titanium doping into LiNbO₃ are shown in Figure 3. The waveguide’s geometry is first delineated on the crystal by a photolithographic process. UV sensitive photoresist is
Figure 2. An optical waveguide directional coupler switch [Alferness (1986)].
Figure 3. Various steps in the fabrication of a titanium rich waveguide in LiNbO$_3$ [Alferness (1986)].
applied to the surface of the crystal and selected regions are exposed by etching away the photoresist solution. Titanium is deposited on the exposed surface either by sputtering or some evaporative process. After the remaining photoresist is dissolved away, titanium is oxidized and diffused into the wafer.

The starting material for the above mentioned waveguide is a single crystal of lithium niobate grown from the congruent composition and poled by cooling the crystal through the Curie temperature in the presence of an electric field. This poling ensures the alignment of the domains in the crystal, leading to the formation of a single domain crystal. The single domain structure is desired to avoid optical scattering by domain walls or grain boundaries. In order to maintain this single domain structure, all subsequent processing including titanium diffusion, should be done below the Curie temperature of lithium niobate. Titanium diffusion lowers the Curie temperature of LiNbO$_3$ below the temperature normally employed for satisfactory diffusion of titanium into LiNbO$_3$. This decrease of the Curie temperature below the processing temperature leads to the destruction of the single domain structure of LiNbO$_3$. The breakdown of the single domain structure leads to the formation of domain walls and an associated loss of transmission quality. Another disadvantage associated with the doping of lithium niobate with titania is the non-uniform contraction in the lattice parameters of lithium niobate crystal. This non-uniform contraction causes strains in the crystal and a subsequent drift in device characteristics during application.
1.2 SIGNIFICANCE OF THE CURIE TEMPERATURE AND COMPOSITION

It is seen from the discussion on the fabrication of titania doped waveguides, that the Curie temperature ($T_c$) determines the temperature at which the dopants can be diffused into the crystal. The diffusion temperature determines the production efficiency and the quality of the waveguide. The most important challenge restricting the application of lithium niobate is this reduction in transmission quality associated with the decrease in the $T_c$ of LiNbO$_3$ on doping with titanium dioxide. Dopants other than titanium dioxide have not been investigated due to the non-availability of solubility information of the dopants in LiNbO$_3$. The effect of the dopants on the ferroelectric properties of LiNbO$_3$, particularly the $T_c$ has not been fully investigated.

This work focused on identifying a dopant for LiNbO$_3$, that does not suffer from some of the drawbacks experienced by the titania doped system. Emphasis of this research was on determining the solid solubility of the different dopants in LiNbO$_3$, the effect of the dopants on the Curie temperature of LiNbO$_3$, and the validity of the different theories currently used to explain the dependence of the Curie temperature on the concentration of dopants.

In order to provide a better understanding of this study and its significance, the next chapter will review the phase diagram, crystal structure, defect chemistry and previous studies on doping of lithium niobate. This will be followed by an experimental section and results of this study will be presented and discussed in the final chapter.
CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 LITHIUM NIOBATE (LiNbO₃)

As mentioned in the first chapter, LiNbO₃ has a very interesting combination of properties such as ferroelectricity, pyroelectricity, piezoelectricity and acousto-optic properties [Pendegrass (1987)]. Some of the attractive properties of lithium niobate (Table 1) include very high spontaneous polarization, high Curie temperature, large electro-optic coefficient and acousto-optic coefficient [Prokhrov and Kuz’minov (1990)].

Table 1. Important properties of LiNbO₃

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordinary index, (n_o)</td>
<td>2.296</td>
</tr>
<tr>
<td>Extraordinary index, (n_e)</td>
<td>2.208</td>
</tr>
<tr>
<td>Birefringence</td>
<td>0.0885</td>
</tr>
<tr>
<td>Electro-optic coefficient</td>
<td>(30 \times 10^{-12} \text{m/V})</td>
</tr>
<tr>
<td>Transparent window</td>
<td>0.4-5 (\mu)m</td>
</tr>
<tr>
<td>Curie Temperature</td>
<td>1210°C</td>
</tr>
</tbody>
</table>
The ordinary index and the extraordinary index indicate that the light travels with different velocities along the two principal axes of lithium niobate. The difference between the two indices is referred to as the birefringence of the crystal. The importance of this quantity in non-linear applications will be discussed in a later section. The transparent window is wide and encompasses the wavelength region for which a silica fiber has its lowest loss (1.3-1.5 \( \mu \text{m} \)). The electro-optical coefficient is high which translates to low control voltages. The \( T_c \) is the highest among all the materials known but depends on the composition and the method of measurement. There is some variation in the Curie temperature value reported in the literature and the reasons for this difference will be highlighted in the section on variation in the properties of LiNbO\(_3\) with Li/Nb ratio.

### 2.2 PHASE DIAGRAM

Lithium niobate is the best studied phase in the Li\(_2\)O-Nb\(_2\)O\(_5\) system. Various researchers have studied the system over the years and the phase diagram has been revised numerous times [Lerner et al. (1968)]. Lithium niobate was thought to be a line compound and crystals of lithium niobate were grown from stoichiometric (equal moles) composition of Li\(_2\)O and Nb\(_2\)O\(_5\). Crystals grown from the stoichiometric composition were assumed to be identical to the composition of the melt. The inhomogeneities in the optical properties and variation in the Curie temperatures from boule to boule led to suspicions of an incongruently melting composition [Fay et al. (1968)]. Figure 4 shows the phase diagram of the Li\(_2\)O-Nb\(_2\)O\(_5\) system. The phase diagram is shown for the end composition of Li\(_2\)CO\(_3\) and Nb\(_2\)O\(_5\), the usual starting components for the preparation of LiNbO\(_3\).
Figure 4. Phase diagram of the Li$_2$O-Nb$_2$O$_5$. The phase diagram is shown for the end composition if Li$_2$CO$_3$, the usual starting component [Reisman et al. (1958)].
Figure 5 is an expanded view of the Li$_2$O-Nb$_2$O$_5$ [Carruthers et al. (1971)] system showing the region of non-stoichiometry in LiNbO$_3$.

Lerner et al. (1968) were the first to investigate the possibility of a LiNbO$_3$ solid solution using lattice parameter measurements. Their study confirmed the existence of a solid solution range for LiNbO$_3$ and they also determined that the maximum melting temperature of LiNbO$_3$ does not occur at the stoichiometric composition but somewhere between 48 to 49 mole% Li$_2$O. The phase diagram was modified to show the existence of LiNbO$_3$ over the range of 48 to 49% Li$_2$O (Figure 5). Carruthers et al. (1971) followed up this study by investigating the non-stoichiometry in lithium niobate using NMR spectroscopy. In their study, they determined the existence of two types of niobium sites, which gave more credence to the existence of some form of non-stoichiometry in lithium niobate. This study also showed that the congruent composition occurs at 48.6 mole% Li$_2$O and the solid solution region at room temperature extends from 48% to 50% Li$_2$O. It was shown by Bridenborg et al. (1970) that crystals grown from 48.6 mole% Li$_2$O do not show any variation in optical properties and this was then assumed to be the congruent composition [Chow et al. (1974)].

Svessend et al. (1973) conducted studies on the range of solid solution for lithium niobate and determined that congruent lithium niobate was not stable at room temperature. Heat treatment of congruent lithium niobate (48.6 mole% Li$_2$O) below 910°C for a prolonged period of time leads to the precipitation of a LiNb$_3$O$_8$ phase and a subsequent loss in transmission quality. The decomposition of lithium niobate was then correlated with the
Figure 5. Li₂O-Nb₂O₅ showing the region of non-stoichiometry in LiNbO₃ [Carruthers et al. (1971)].
change in optical transmission quality. This result suggests that congruent lithium niobate composition is not a single phase at room temperature. It should be pointed out here, that in single crystals of lithium niobate, no second phase has been observed at room temperatures for cooling rates of approximately 100°C/hour.

The most recent attempt to determine the composition of congruent lithium niobate was done by O'Bryan et al. (1985). In that study the congruent composition was determined by correlating the crystal growth compositions with the Curie temperature of the samples quenched from a melt before and after crystal growth and for various sections of the crystals grown from the melt. According to this theory, if mixing is complete in the liquid and diffusion in the solid is negligible, then

\[ k = \frac{C_s}{C_l} \]  

(2.1)

where \( k \) is the distribution coefficient of lithium oxide while \( C_s \) and \( C_l \) are the concentration of lithium oxide in the solid and the liquid. The congruent composition corresponds to the composition at which \( k \) equals 1. O'Bryan et al. calculated the distribution coefficient for different starting composition of lithium oxide in the melt. Table 2 gives a better understanding and the results of their approach.
Table 2. Crystal growth results [[O'Bryan et al. (1985)]]

<table>
<thead>
<tr>
<th>Composition (mole% Li$_2$O)</th>
<th>Distribution coefficient (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>Solid</td>
</tr>
<tr>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>47.0</td>
<td>45.45</td>
</tr>
<tr>
<td>48.0</td>
<td>47.44</td>
</tr>
<tr>
<td>48.20</td>
<td>47.73</td>
</tr>
<tr>
<td>48.40</td>
<td>48.21</td>
</tr>
<tr>
<td>48.60</td>
<td>48.80</td>
</tr>
<tr>
<td>48.80</td>
<td>49.32</td>
</tr>
<tr>
<td>49.00</td>
<td>49.86</td>
</tr>
</tbody>
</table>

The lithium concentration was calculated from Curie temperature measurements. It is seen from the table, that the distribution coefficient approaches 1 between 48.4 and 48.6 mole% Li$_2$O. The congruent composition (k=1) was found to be at 48.45 mole% Li$_2$O from a plot of the distribution coefficient and mole% Li$_2$O in the initial melt. The currently accepted value for the congruent composition based on this study is 48.45 mole% lithium oxide.
Bordui et al. (1992) attempted to refine the phase boundary of lithium rich lithium niobate. Lithium niobate crystals of various compositions were prepared by vapor transport equilibration of congruent lithium niobate with lithium rich and lithium poor compositions. The resulting crystals were characterized by the Curie temperature and the temperature for non-critical phase matching of second harmonic generation. It was determined by their study that the phase boundary composition at 1100°C was 50.02 mole% Li₂O, on the lithium rich side. The accuracy of measurement considering all possible error sources was determined to be 0.01 mole% Li₂O. This is the first reported existence of lithium niobate in the lithium rich side of the phase diagram and is in conflict with all of the previously reported studies.

This brief review points out to the difficulty in studying the lithium niobate system. Some of the discrepancies arise because of the difficulty in determining the exact amount of lithium. Lithium being a light element is not amenable for easy quantification and lithium also is prone to vaporization. Some of these difficulties will be amplified as we begin to discuss the defect structure of lithium niobate.

2.3 CRYSTAL STRUCTURE OF LITHIUM NIOBATE

The crystal structure of lithium niobate was initially thought to be similar to that of ilmenite. The discovery of ferroelectricity in lithium niobate by Megaw (1968) ruled out the possibility of centrosymmetric ilmenite structure for lithium niobate. The structure of lithium niobate was revised and an R3C space group was proposed without
determining the ion positions. The structure was extensively studied in the 1960’s by Abrahams and his co-workers and they confirmed the R3C symmetry using a high quality single crystal and x-ray diffraction techniques.

The lithium niobate structure can be described in terms of either a hexagonal or a rhombohedral basis. The hexagonal unit cell consists of six formula units and the lattice parameters are \( a_h = 5.14829 \pm 0.0002 \, \text{Å} \) and \( c_h = 13.8631 \pm 0.0004 \, \text{Å} \). The rhombohedral unit cell contains two formula units with \( a = 5.4944 \, \text{Å} \) and \( \alpha = 52^\circ \). The hexagonal unit cell has a distorted hexagonal packing of oxygen atoms with cations in \( 2/3 \) of the octahedral sites. Figure 6 shows the structure of lithium niobate with planes showing the oxygen ions and the cations sitting between the planes. The cations are arranged with niobium ions near the center and lithium more off center. For easier understanding, the structure of lithium niobate is compared to ilmenite and \( \alpha \)-alumina in Figure 7. In \( \alpha \)-alumina both the cations are alike, but in lithium niobate and ilmenite there are two kinds of cations and their stacking sequence is different.

2.4 DEFECT STRUCTURE OF LITHIUM NIOBATE

As discussed earlier LiNbO\(_3\) exists over a range of composition (48-50 mole% Li\(_2\)O). Currently the greatest interest is in congruent LiNbO\(_3\) from which single crystals are grown. As congruent lithium niobate is inherently defective (lithium deficient), there is some interest in stoichiometric LiNbO\(_3\) for optical applications. In this section we will discuss the defect chemistry of lithium niobate.
Figure 6. The crystal structure of LiNbO$_3$ [Haycock and Townsend (1986)].
Figure 7. Cation stacking sequence in LiNbO$_3$ [Chang et al. (1987)].
Kroger-Vink notation is used in describing defect equilibria throughout this document. In the Kroger-Vink notation, the superscript denotes the relative charge of the site and the subscript the ion at the site in a perfect lattice.

2.4.1 Schottky and Frenkel disorder in LiNbO$_3$

Donneberg et al. (1991) studied the defect chemistry of lithium niobate using computer simulation. They used a shell model in which the energy was minimized with respect to all ionic cores for both the perfect and the defect lattice. In their calculation the crystal relaxation around the crystal was also taken into account. A second approach was also used in which the macroscopic crystal constants were fitted with experimental values. Using both the approaches Donnenberg et al. (1991) calculated the formation energies for the Schottky and Frenkel defects in LiNbO$_3$. It was concluded from the study of Donnenberg et al. (1991) that the energy for the formation of Schottky and Frenkel defects of niobium and oxygen were high and thus these defects should play relatively a minor role in LiNbO$_3$. The energy for the formation of Schottky defects in LiNbO$_3$ are comparable to the formation energies of Schottky defects in BaTiO$_3$. Schottky defects are insignificant in BaTiO$_3$ and there seems to be no proof for the existence of these defects in LiNbO$_3$ either. Frenkel disorder should play a major role due to the small binding energy of lithium. In fact lithium niobate has been found to have an appreciable ionic conductivity and the measured activation energy for ionic conductivity of LiNbO$_3$ is 1.1 eV [Smyth (1983)]. Thus there seems to be strong evidence for the existence of Frenkel defects of lithium in LiNbO$_3$. 
2.4.2 Defects as a function of non-stoichiometry

Initial attempts to describe the non-stoichiometry in LiNbO₃ started from efforts to understand the variation in the second harmonic phase matching temperature with variation in stoichiometry. Fay et al. (1968) were the first to study this problem and proposed a lithium loss model to account for non-stoichiometry.

\[
2\text{Li}^+ + \text{O}_0^x \leftrightarrow \text{Li}_2\text{O} + 2\text{V}_{\text{Li}}^\text{l} + \text{V}_0^2^+ \quad (2.2)
\]

According to this model, loss of lithium is accompanied by vacancies at the lithium and oxygen sites. This oxygen vacancy model could not account for the experimentally observed increase in density of LiNbO₃ with Li₂O loss. Based on this observation, Lemer et al. (1968) proposed a model with completely filled oxygen and niobium lattices but with vacancies at some lithium sites.

\[
6\text{Li}^+ + \text{O}_0^x + 3\text{Nb}_{\text{Nb}}^x \leftrightarrow 3\text{Li}_2\text{O} + 4\text{V}_{\text{Li}}^\text{l} + \text{Nb}_{\text{Li}}^4^+ \quad (2.3)
\]

The congruent composition according to equation 2.3, corresponds to 3.66% lithium sites being vacant and 0.92% lithium sites occupied by niobium ions. Lerner's model assumes complete oxygen and niobium sub-lattice and the formula for LiNbO₃ according to this model is expressed as \( \text{Li}_{(1.5x)}(\text{Nb}_{\text{Li}})_x(\text{V}_{\text{Li}})_4x\text{NbO}_3 \). This model was widely accepted until the high precision single crystal x-ray diffraction work of Abrahams et al. (1986), which will be discussed in detail later.
Peterson and Carnevale (1972) were the first to experimentally observe the existence of two different environments for niobium ions. Using NMR techniques they found niobium on niobium sites and a second site accounting for 6% of the niobium ions. Based on this observation they proposed that every vacant lithium site is occupied by niobium ions leaving vacancies at the niobium sites. Nassau and Lines (1970) disagreed with niobium on lithium sites and proposed the following stacking fault model to account for lithium deficiency. Lithium loss is accompanied by a short linear section containing an incorrect sequence of cations. The cation stacking fault accounts for the loss of one layer of lithium atoms resulting in niobium rich stoichiometries. The formula for LiNbO$_3$ is expressed as Li$_{(1.5x)}$Nb$_{(1+x)}$O$_3$ according to this model. There is not any evidence for such a faulting mechanism either by x-ray diffraction or transmission electron microscopy examination [McCoy (1990)].

2.4.3 Abrahams and Marsh Defect Model

The most detailed and conclusive work on the defect structure of congruent lithium niobate was carried out by Abrahams and Marsh (1986). They characterized single crystals of LiNbO$_3$ using high precision x-ray diffraction (XRD) and measurement of density. They proposed the following defect model to account for lithium deficiency in LiNbO$_3$

1. Anion lattice to be complete (i.e., no oxygen vacancies).
2. All the lithium sites are occupied either by Li$_{Li}$ or Nb$_{Li}$ sites and
3. Vacancies occur at niobium sites.
The key element of this model is that as the composition becomes poorer in lithium, niobium atoms will substitute on lithium sites until all the lithium sites are completely filled and vacancies will be simultaneously created at the niobium sites. For a crystal of congruent composition \( \text{Li}_{0.94}\text{Nb}_{1.012}\text{O}_3 \) the site occupancy for

- **Lithium Sites** 94.1% Li ions  
  5.9% Nb ions

- **Niobium Sites** 95.3% Nb ions  
  4.7% Vacancies

- **Oxygen sites** 100.0% Oxygen ions

Each missing lithium ion is replaced by a niobium ion leaving a Schottky vacancy and congruent lithium niobate is represented by the formula \( (\text{Li}_{1.5x}\text{Nb}_x)\text{Nb}_{1-4x}\text{O}_3 \). Densities calculated from this model assuming complete oxygen sub-lattice and vacancies at the cation sites, match well with the experimental densities.

### 2.4.4 Chang, Mehta and Smyth Model

Based on the Abrahams and Marsh model Chang et al. (1987) have developed the concept of defect complex to account for the deficiency of lithium. Figure 8 shows the cation stacking sequence in lithium niobate, corundum and ilmenite. Figure 8(c) represents the defect structure as given by the Abrahams and Marsh model and the misplaced niobium results in three consecutive sites occupied by niobium ions.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>Nd</th>
<th>Nd</th>
<th>Nd</th>
<th>Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A</td>
<td>B</td>
<td>Li</td>
<td>Li</td>
<td>Li</td>
<td>Li</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>B</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>A</td>
<td>-Nd-</td>
<td>Li</td>
<td>Li</td>
<td>Li</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>B</td>
<td>-</td>
<td>-Nd-</td>
<td>-Nd-</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>A</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
</tbody>
</table>

Corundum: LiNbO$_3$, Ilmenite
(a) (b) (c) (d) (e)

Figure 8. The different defect models to account for charge imbalance in LiNbO$_3$ [Chang et al. (1987)].
According to Chang et al., 8(c) is an energetically unfavorable situation and this can be relieved by placing the niobium vacancy next to the displaced niobium as shown in Fig. 8(d), thereby creating a defect complex. The reaction for lithium loss can then be written as

\[
6\text{Li}_\text{Li} + 3\text{O}^* + 3\text{Nb}_{\text{Nb}}^* \rightleftharpoons 3\text{Li}_2\text{O} + 4(\text{Nb}_{\text{Li}}\text{V}_{\text{Nb}})^{1^-} + \text{Nb}_{\text{Li}}^{4^+}
\]  

(2.4)

where the defect combination in parentheses represents a defect complex. If the defects in the bound complex exchange positions [Figure 8(e)], it results in a simple lithium vacancy, leading to the Lerner et al. (1968) defect model. The complex actually corresponds to an ilmenite stacking sequence containing a lithium vacancy. According to Chang et al. (1987) the lithium niobate stacking sequence and ilmenite stacking sequence are energetically equivalent and they draw proof for this from the preparation of lithium niobate in the ilmenite structure by a low temperature ion exchange technique [Kumada et al. (1985)].

2.4.5 Computer Simulation

Computer simulation studies have again been used to calculate defect energies for non-stoichiometric LiNbO₃. Any one of the following equations could account for the loss of lithium from stoichiometric LiNbO₃.
2Li\textsubscript{Li} + \text{O}_0^* \leftrightarrow \text{Li}_2\text{O} + 2\text{V}_{\text{Li}}^\text{Li} + \text{V}_{\text{O}}^0 \quad \text{Oxygen Vacancy Model (2.5a)}

6\text{Li}_\text{Li}^{\text{Li}} + \text{Nb}_{\text{Nb}}^{\text{Nb}} + 3\text{O}_0 \leftrightarrow 4\text{V}_{\text{Li}}^\text{Li} + \text{Nb}_{\text{Li}}^{\text{Li}} + 3\text{Li}_2\text{O} \quad \text{Lithium Vacancy Model (2.5b)}

6\text{Li}_\text{Li}^{\text{Li}} + 3\text{O}_0 + 5\text{Nb}_{\text{Nb}}^{\text{Nb}} \leftrightarrow 4\text{V}_{\text{Nb}}^\text{S'Nb} + 5\text{Nb}_{\text{Li}}^{\text{Li}} + 3\text{Li}_2\text{O} \quad \text{Abrahams Model (2.5c)}

Slight modification of the last equation gives

6\text{Li}_\text{Li}^{\text{Li}} + 3\text{O}_0 + 5\text{Nb}_{\text{Nb}}^{\text{Nb}} \leftrightarrow 4(\text{V}_{\text{Nb}}^\text{S'Nb} + \text{Nb}_{\text{Li}}^{\text{Li}}) + \text{Nb}_{\text{Li}}^{4+} + 3\text{Li}_2\text{O} \quad \text{Smyth Model (2.5d)}

For the Abrahams and Marsh model to be energetically favorable

\[ E_{\text{Nb}_{\text{Li}}^{4+}} + E_{\text{V}_{\text{Nb}}^\text{S-}} \leq E_{\text{V}_{\text{Li}}^-} \quad (2.6) \]

For the defect complex to be energetically favored

\[ E_{\text{Complex}} + E_{\text{V}_{\text{Nb}}^\text{S-}} \leq E_{\text{V}_{\text{Li}}^-} \quad (2.7) \]

It was determined by Donnenberg \textit{et al.} (1991) from their energy model calculations that neither equation 2.6 or 2.7 was satisfied. The contradiction between the energetic and x-ray results is accounted for by an ilmenite like stacking sequence in LiNbO\textsubscript{3}. As the lattice energy per unit cell is only slightly less favorable (about 0.3\%) between the normal LiNbO\textsubscript{3} and the ilmenite stacking, an intermixing between the two stacking sequence is proposed as the most likely defect mechanism.
2.4.6 Recent Developments

Support for the lithium vacancy model also comes from a recent study of Iyi et al. (1992). They studied four different compositions from stoichiometric lithium niobate to lithium deficient lithium niobate (Li/Li+Nb = 0.47) by single crystal x-ray diffraction and neutron diffraction. A lithium site vacancy model expressed as \((\text{Li}_{1.5x}\text{Nb}_{x}\text{V}_{4x})\text{NbO}_3\) and a niobium site vacancy model expressed as \((\text{Li}_{1.5x}\text{Nb}_{5x})(\text{Nb}_{1.5x}\text{V}_{4x})\text{O}_3\) were chosen as the possible defects in the refinement process. The refinement results indicated that the amount of niobium occupancy independent of composition, thus indicating lithium vacancies as the compensating defect. Iyi et al. (1992) attributed the observed differences between their work and the work of Abrahams and Marsh to the following factors.

In single crystal x-ray diffraction low scattering factors of lithium compared with niobium makes information on lithium uncertain. Also the correction for extinction, thermal motion and scattering factor affect the final occupation. Neutron diffraction gives better accuracy as the scattering lengths for Li and Nb are very different and can give a clear measure of the occupancy at the lithium site. In the study by Abrahams and Marsh, the stoichiometric lithium niobate was made by ion-diffusion method while the congruent lithium niobate was made from the melt. This different processing condition alone could account for the observed difference in the structure of lithium niobate between the two studies.
The same conclusion of lithium vacancies being the predominant defect was arrived at by Wilkinson et al. (1993) by powder x-ray diffraction work on lithium niobate samples. Powder diffraction is advantageous because it avoids the difficulties due to extinction that arise in the single crystal diffraction work. This study again concluded that the observed difference with the work of Abrahams and Marsh could arise from different processing conditions.

More recent NMR measurements [Blumel et al. (1994)] have not been able to distinguish between Nb\textsubscript{Li} site and Nb\textsubscript{Nb} sites. Blumel et al. (1994) suggest that the second resonance observed in the study by Peterson was an artifact, due to the low magnetic field strength used. Based on the inability to determine a second site for niobium, these authors suggest that a vacancy of lithium is the likely charge compensation mechanism. Douglass and Peterson (1986), the original proposers of niobium on the lithium site model, reexamined their data using simulation studies and suggested that the interpretation of Nb NMR data is less straightforward than thought previously.

Birnie (1993) has recently reviewed the defects in lithium niobate. For charge neutrality the following equation should hold good at any temperature.

\[
4\text{[Nb}\textsubscript{Li}\textsuperscript{4+}] \Leftrightarrow \text{[V}\textsubscript{Li}\textsuperscript{5\textdagger}\text{-}] + [\text{(Nb}\textsubscript{Li}\text{V}\textsubscript{Nb})\textsuperscript{1\textdagger\text{-}}] + 5\text{[V}\textsubscript{Nb}\textsuperscript{5\textdagger\text{-}}] \quad (2.8)
\]
Equation (2.8) can be approximated, with one type of defect being the dominant defect at different temperature ranges. Table 3 shows the Browers approximation of equation 2.8 at low temperature and high temperature.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Low Temperature</th>
<th>High Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Nb}^f_{\text{Li}}] \rightleftharpoons 4[\text{V}_{\text{Li}}])</td>
<td>Disallowed (Abrahams and Marsh study)</td>
<td>Preferred (Rapid lithium diffusion)</td>
</tr>
<tr>
<td>(5[\text{Nb}^4_{\text{Li}}] \rightleftharpoons 4[\text{V}^5_{\text{Nb}}])</td>
<td>Preferred (Coulombic attraction of defects during cooling)</td>
<td>Possible ( Likely as transition stage from low to high temperature)</td>
</tr>
<tr>
<td>([\text{Nb}^4_{\text{Li}}] \rightleftharpoons 4([\text{Nb}^2_{\text{Li}}, \text{V}_{\text{Li}}])^{1+})</td>
<td>Not Preferred (High charge of separate point defects)</td>
<td>Not Likely (Diffusion of lithium much more rapid than niobium)</td>
</tr>
</tbody>
</table>

Dunbar concluded from Table 3 that the defect clusters dominate at lower temperatures with a gradual transition towards free lithium vacancies at high temperatures. Although the model of Abrahams and Marsh is widely accepted, the defect structure of lithium niobate is not clearly understood. There seems to be increasing evidence against the model of Abrahams and Marsh. As more work is done on lithium niobate, more questions arise about the defect structure of LiNbO₃.
2.4.7 Oxygen Vacancies

There have been reports on vacancies of oxygen occurring in LiNbO$_3$. Optical absorption peaks [Sweeny et al. (1983)] at 760 nm and 500 nm have been assigned to oxygen vacancies. As mentioned previously the density of LiNbO$_3$ increases with reduction and creation of oxygen vacancies is not consistent with this observation. It is inconsistent to propose one set of defects to account for Li$_2$O deficiency and a different for oxygen loss [Smyth (1983)]. The overwhelming evidence is that vacancies of oxygen are not present in any significant quantity except when irradiation with high energy electron is applied.

2.5 PROPERTIES OF LiNbO$_3$ DEPENDENT ON THE Li/Nb RATIO

As discussed in the previous section the Li/Nb ratio determines the quality of crystals, defect structure and the performance of devices. Several properties of lithium niobate are strongly dependent on the Li/Nb ratio in the crystal. The properties and the nature of their dependence on the Li/Nb ratio are shown in Table 4.
Table 4. Properties dependent on the Li/Nb ratio [Rauber (1978)].

<table>
<thead>
<tr>
<th>Dependence</th>
<th>Measured quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak</td>
<td>Lattice Parameters</td>
</tr>
<tr>
<td></td>
<td>Density</td>
</tr>
<tr>
<td></td>
<td>Refractive Index</td>
</tr>
<tr>
<td>Strong</td>
<td>Curie temperature</td>
</tr>
<tr>
<td></td>
<td>Birefringence</td>
</tr>
<tr>
<td></td>
<td>Phase-matching temperature</td>
</tr>
</tbody>
</table>

Determination of the Li/Nb ratio is very difficult as lithium is a light element and not amenable to many of the spectroscopic techniques. The most direct method to determine the molar ratio of Li/Nb would be through quantitative chemical analysis. Chemical analysis is almost impossible to a high precision [Arizmendi (1988)] because of the large difference in atomic masses of lithium and niobium and difficulty of dissolving lithium niobate [Rauber (1978)]. The sensitivity from chemical analysis in the few cases it has been attempted is at best about $10^{-2}$ moles. So some of the properties that are strongly dependent on the Li/Nb ratio are used to determine the composition of the crystal.

2.5.1 The Curie Temperature

Measurement of the Curie temperature using a DTA or dielectric constant is the most widely used method to determine the lithium concentration of LiNbO$_3$. The advantage for the determination of $T_c$ using DTA include simplicity of operation, no elaborate sample preparation and the ability to work with powders.
Figure 9. Variation in the $T_c$ with lithium concentration in LiNbO$_3$ [O'Bryan et al. (1985)].
Figure 9 shows the variation in \( T_c \) as a function of lithium concentration in lithium niobate [O'Bryan et al. (1985)]. The three different curves indicate the correlation between the Curie temperature and the lithium concentration as observed by different authors. The linear least square fit by O'Bryan et al. (1985) enables \( T_c \) to be expressed as a function of the lithium concentration \( C \). Here \( C \) refers to the lithium concentration in the single phase region of \( \text{LiNbO}_3 \) and lies between 47 and 50 mole% \( \text{Li}_2\text{O} \).

\[
T_c = -637.30 + 36.70 C \quad (2.9)
\]

A quadratic least square fit gives a better fit of the observed data.

\[
T_c = 9095.2 -369.05C + 4.228 C^2 \quad (2.10)
\]

As the composition approaches stoichiometry \((\text{Li/Nb}=1)\) the Curie temperature approaches the solidus curve (Figure 4) and intersects it before reaching the stoichiometric composition. The enthalpy associated with the melting masks the weak second order Curie transition and thus it is difficult to measure \( T_c \) near the stoichiometric composition using DTA. Dilatometric measurements were used to measure [Gallagher et al. (1985)] \( \text{dL/L} \) and \( T_c \) was determined from the change of slope as shown in Figure 10.

There is a substantial variation in the \( T_c \) of stoichiometric lithium niobate depending on the method of measurement or estimation of the Curie temperature. Curie temperature
Figure 10. Determination of $T_c$ using a dilatometer [Gallagher and O'Bryan (1985)].
measurements using a dilatometer (Figure 10) gives a value of 1198°C. The value of $T_c$ for the stoichiometric composition using a DTA is arrived at by extrapolating from the linear portion of the $Li_2O$ vs. $T_c$ plot to 50% $Li_2O$ composition. This method of determining $T_c$ gives a value in the range of 1192°C to 1204°C [Guenais et al. (1981)]. But the most widely used value for the $T_c$ of stoichiometric $LiNbO_3$ in literature is about 1210°C. This value was reported by Nassau et al. (1966) in one of the early papers on $LiNbO_3$. Nassau arrived at this value by dielectric measurement on various compositions in the $LiNbO_3$ - $LiTaO_3$ system. As he was able to measure $T_c$ only for compositions up to 80% $LiNbO_3$, he extrapolated the $T_c$ vs. composition curve to obtain the $T_c$ of pure $LiNbO_3$. Although it is now known this value is higher than most recent measurements, Nassau’s paper is widely referred to in literature.

The sensitivity of $T_c$ to lithium concentration is about $4 \times 10^{-3}$ moles. The disadvantages of DTA include the requirement to make the measurement at high temperature, which might lead to problems of loss of lithium and the inability to measure $T_c$ close to stoichiometric composition.

2.5.2 The phase matching temperature

The laser source changes the refractive index of $LiNbO_3$ and causes the incident light to be emitted with fundamental, second harmonic (half the wavelength of incident light) and DC components. Second harmonic generation (SHG) arises from non-linear effects
introduced into the crystal by high energy laser sources. Lithium niobate is an efficient second harmonic generator and is used to generate visible light from infra-red sources.

Phase matching temperature ($T_{pm}$) is the temperature at which LiNbO$_3$ is efficient as a second harmonic generator (SHG) [Bridenbaugh et al. (1970)]. The phase matching temperature increases smoothly with lithium concentration ($C$) within the solid solution region and a cubic polynomial fits the data well [Jundt et al. (1992)].

$$C = 48.35 + 8.7 \times 10^{-3} T_{pm} + 2.1 \times 10^{-6} T_{pm}^2 - 4.7 \times 10^{-8} T_{pm}^3 \quad (2.11)$$

The phase matching temperature is the most sensitive parameter to measure Li/Nb ratio. A change of composition of 1 mole% causes a 150°C change in $T_{pm}$. The phase matching temperature has a sensitivity of about $\Delta(Li/Nb) = 5 \times 10^{-4}$. This measurement can be done only on single crystals and the setup for this measurement is very expensive and cumbersome.

A number of other methods including the measurement of the refractive index [Bergman et al. (1968)], and lattice parameters [Lerner et al. (1968)] have been used to determine the Li/Nb ratio. Figure 11 shows the variation of refractive index as a function of the Li/Nb ratio. The extraordinary index is strongly affected by the Li/Nb ratio, while the ordinary index does not change with lithium concentration. So birefringence ($n_e - n_o$) is used to characterize the composition of the LiNbO$_3$ crystal.
Figure 11. Variation in the refractive index as a function of Li/Nb ratio [Bergman et al. (1968)].
2.6 ROLE OF DOPANTS IN LITHIUM NIOBATE

Many of the applications of lithium niobate depends on the effect of foreign ions on the lattice of lithium niobate. These foreign ions modify the optical properties of the matrix and enable it to be used in various applications. Some important examples follow:

(1) Optical waveguides are created in lithium niobate by diffusion of titanium into lithium niobate.

(2) Photorefractive properties can be controlled by transition ions and MgO dopants.

(3) Rare-earth ion dopants are used to produce solid-state lasers from lithium niobate.

In order to fully appreciate the significance of dopants, the role of dopants in waveguide and photorefractive applications is discussed.

2.6.1 Optical Waveguides

There are a number of methods for fabricating optical waveguides from lithium niobate, including lithium outdiffusion [Fukuma et al. (1981)], proton exchange [Jackel et al. (1983)] and by indiffusion of alioivalent dopants [Arvidsson et al. (1985)]. Titanium indiffused waveguides are the most advanced and have the lowest loss among the available waveguides. The various steps involved in the manufacture of titanium waveguides was discussed previously. During the process of waveguide formation, titanium diffuses into LiNbO$_3$ to form a Li(Nb, Ti)O$_3$ solid solution. This solid solution has a higher refractive index [Tamir (1988)] and causes total internal reflection of 1.3 μm
and 1.5 μm optical signals used in silica fibers. Figure 12 shows the variation of refractive index with titanium doping.

2.6.2 Photorefractive Effect

Photorefractive effect or its negative aspect called optical damage refers to the inhomogenieties caused in the refractive index of a crystal by laser beams. This effect, although used as an optical storage mechanism has undesirable influence on optical devices. The index change induced by the laser beams blurs the wavefront of the beams and affects coherency [Sweeney et al. (1985)]. The susceptibility of LiNbO₃ to laser damage has been correlated with the iron content of the crystal. [Peterson et al. (1973)]. Attempts have been made to reduce the levels of impurity and the oxidation state of the impurity to reduce laser damage in lithium niobate. Addition of dopants to decrease laser damage is a much less expensive option than to work with ppb impurities.

The application of titanium doped lithium niobate is also limited by the photorefractive effect and limits the power that can be carried in a Ti: LiNbO₃ waveguide at visible wavelengths [Sjoberg et al. (1988)]. Growing crystals from a lithium rich melt leads to a decrease in optical damage but it is difficult to grow good quality crystals from a lithium rich melt. Thus extensive work has been done on identification of suitable dopants to reduce laser damage. LiNbO₃ doped with 4.6% MgO was able to withstand about 100 times as much optical intensity as undoped lithium niobate [Bryan et al. (1985)].
Figure 12. The refractive index change in LiNbO$_3$ with titanium concentration [Tamir (1988)].
improvement has been correlated to the increase in photoconductivity of lithium niobate with MgO doping.

2.7 ROLE OF DOPANTS ON THE PROPERTIES OF LiNbO₃

There have been various studies on lithium niobate doped with aliovalent impurities. This section will review the effect of dopants on the properties of lithium niobate with specific reference to the defect structure and the Curie temperature. One of the disadvantages of the different studies is the variation in the composition of the starting crystal itself. The concentration of the dopants and lithium in the crystal is different from that of the melt and the lithium composition of the crystal also varies as a function of the dopant concentration. Thus, caution is recommended in interpreting the results.

2.7.1 Titanium Doping

Guenaias et al. (1981) were the first to study systematically the variation in the Curie temperature and lattice parameter as a function of titanium concentration on powdered samples. The Curie temperature of the titanium doped samples decreased substantially with titanium doping. The Curie temperature variation was correlated with $R_e$ where $R_e = 0.954/(0.954+1.0092+X)$ and $X$ is the titanium concentration in LiNbO₃. $R_e$ is nothing but the ratio of the total number of lithium sites occupied to the total number of cation sites occupied. Figure 13 shows the variation of $R_e$ for titanium doped and undoped lithium
Figure 13. The variation in the $T_c$ of LiNbO$_3$ as a function of titanium concentration [Guenais et al. (1981)].

D1 Guenais et al. (1981)
D2 Carruthers et al. (1971)
niobate. The two lines coincide indicating that the Curie temperature variation is very small when the Nb$^{5+}$ cations are replaced by Ti$^{4+}$ cations at a specified $R_a$. Based on this study it was concluded that oxygen vacancies were the compensating defects on titanium doping in lithium niobate. It should be pointed out here that there is no proof for the existence of oxygen vacancies in titanium doped lithium niobate and yet oxygen vacancies are proposed to explain the observed behavior.

The most comprehensive study of titanium doping in lithium niobate has been carried out by Gallagher et al. (1988). This study used powder samples and thus there was no variation in lithium and dopant concentration from sample to sample as in the case of single crystal samples. The variation in the properties of lithium niobate as a function of titanium concentration was explained on the basis of the Abrahams and Marsh model. The ratio of cations to anions in lithium niobate is 2:3 while in titanium dioxide (TiO$_2$) the ratio is 1:2. Thus the addition of TiO$_2$ to LiNbO$_3$ should introduce cation vacancies into the structure of LiNbO$_3$ and should have a similar effect as decreasing the lithium concentration. According to Gallagher et al., for a single phase lithium niobate with the formula Li$_y$Nb$_{1-y}$Ti$_2$O$_{2.5-2y+2z}$

Number of A sites = Number of B sites = $(2.5-2y+2z)/3$ \hspace{1cm} (2.12a)

$\#$ of vacant A sites = $\#$ of B sites transferred to A = $(2.5-2y+2z)/3 - y$ \hspace{1cm} (2.12b)

Number of B sites vacant = $(2.5-2y+2z)/3 - (1-y) + ((2.5-2y+2z)/3 - y) - z$ \hspace{1cm} (2.12c)

Cation vacancy concentration = $(2-4y+z)/3$ \hspace{1cm} (2.12d)
Based on this relationship the cation vacancy concentration (CV)
In the undoped lithium niobate (z=0)

\[ CV = 2 - 4y/3 \]  \hspace{1cm} (2.12c)

Stoichiometric lithium niobate (y=0.5)

\[ CV = z/3 \]  \hspace{1cm} (2.12f)

and in congruent lithium niobate (y=0.4845)

\[ CV = (0.06201 + z)/3 \]  \hspace{1cm} (2.12g)

Figure 14 shows the variation of \( T_c \) as a function of cation vacancy concentration for
titanium doped congruent and stoichiometric lithium niobate. It can be seen that \( T_c \) is a function of cation vacancy concentration alone and is independent of the source of the vacancy. It was concluded from this study that the cation vacancy controls the Curie temperature and is mathematically expressed as the result of their least square fit

\[ T_c (^\circ\text{C}) = 1204 - 3280 \times (\text{CV}) \]  \hspace{1cm} (2.13)

Introducing cation vacancies alters the lattice parameter and the variation in lattice parameter as a function of CV is shown in Figure 15. The a axis cell parameter shows a significant reduction as a function of cation vacancy concentration, while the c the axis cell parameter does not show a significant variation. This anisotropic variation in lattice
Figure 14. The variation in the Curie temperature as a function of the cation vacancy. [Gallagher and O'Bryan (1988)].
Figure 15. The variation in the lattice parameter as a function of the cation vacancy. [Gallagher and O'Bryan (1988)].
parameter results in strains in the resulting waveguide and the relaxation of strains in application leads to a drift in device performance. Although the lithium niobate doped with titania has been extensively studied, the site occupied by titani has not been established. There are hardly any reactions proposed for the incorporation of dopants in lithium niobate due to the many different defects species possible in the system.

Two possible reactions that can occur on doping LiNbO₃ with TiO₂ is given below.

\[
\begin{align*}
3\text{TiO}_2 + 2\text{Nb}^{4+}_{\text{Li}} & \iff 3\text{Ti}^{3+}_{\text{Li}} + 2\text{Nb}^{5+}_{\text{Nb}} + V^{1-}_{\text{Li}} + 6O^{5-} & (2.14 \text{ a}) \\
3\text{TiO}_2 + 2\text{Nb}^{6+}_{\text{Nb}} & \iff 3\text{Ti}^{5+}_{\text{Nb}} + 2\text{Nb}^{4+}_{\text{Li}} + V^{5-}_{\text{Nb}} + 6O^{3-} & (2.14 \text{ b})
\end{align*}
\]

It is seen that both reactions result in charge compensation. No reliable method has been developed to determine the site occupancy of the dopant and the site in which vacancies are introduced. The above two reactions are only two of the many possible solutions. The difficulties associated with determining the site occupancy of the dopants and coming up with the consistent doping reactions will be discussed in later sections.

2.7.2 Magnesium Oxide

Magnesium oxide doping should result in effects opposite to that of doping with TiO₂. The cation to anion ration in MgO is 1:1 while in lithium niobate the ratio is 2:3. Thus when three oxygen ions are introduced in LiNbO₃ through MgO doping, the oxygen
brings with it 3 magnesium cations. This introduction of excess cations should annihilate the inherent cation vacancies present in LiNbO$_3$. If the $T_c$ is a function of the cation vacancy concentration as discussed earlier in the case of titania doping, the Curie temperature of LiNbO$_3$ should increase on doping with MgO. One of the drawbacks of this logic is that it rules out all other (oxygen vacancies or holes) charge compensating mechanisms other than annihilation of cation vacancies.

Grabmaier et al. (1986, 1991) have studied the properties of lithium niobate with magnesium doping. Single crystals of lithium niobate of various compositions were used in that study. One of the unique features of that study was the actual determination of lithium and magnesium concentration in the grown crystal. It was concluded that the lithium concentration of the crystal decrease with MgO doping and the distribution coefficient of MgO between the melt and the crystal was found to be 1.2.

Figure 16 shows the variation of lithium concentration and vacancy concentration as a function of magnesium doping. The lithium concentration decreased with magnesium doping while the concentration of cation vacancies actually increased with magnesium concentration. Figure 17 shows the variation in Curie temperature with the MgO content of the crystal without taking into account the lower concentration of the lithium. From figures 16 and 17 it can be seen that the Curie temperature actually increases with the increase in concentration of vacancies.
Figure 16. The variation in the lithium and cation vacancy concentration in LiNbO$_3$ on doping with MgO [Grabmaier (1991)].
Figure 17. The variation in $T_c$ on doping LiNbO$_3$ with MgO [Rossner et al. (1989)].
Grambier et al. (1991) attribute the Curie temperature to be a function of only the vacancy concentration in the niobium sites. According to Grabmaier et al. (1991), the long range dipole interaction, which is mostly caused by Nb-O chains, becomes stronger or weaker depending on the presence of either ions or vacancies at the niobium sites. As a result of this change in occupancy, the frequency of the transverse optical phonon which determines the ferroelectric properties is lowered and the Curie temperature is increased. There is no explanation for the dependence of the Curie temperature on the transverse optical phonon or neither is there any reference to any other article relating the Curie temperature and optical phenomenon. The above reason for the change in the Curie temperature is thus unsubstantiated.

Thus the variation in the Curie temperature for the magnesium doped lithium niobate is explained based on the niobium site occupancy. For the incorporation of small amounts of magnesium, Mg replaces Nb_L sites. Above a threshold level of magnesium incorporation, lithium vacancies are formed in addition to transfer of niobium on lithium sites to niobium sites. This results in an increase in the Curie temperature accompanied by an increase in the cation vacancy concentration. Beyond 4.5 mole% magnesium, all niobium vacancies are occupied and magnesium is incorporated in both lithium and niobium sites. This model explains the observed phenomenon but does not give an explanation for charge compensation in the early stages of magnesium incorporation.

There have been numerous other studies with MgO doping or substitution in lithium niobate [Zhou et al. (1991), Hu et al. (1991)]. All of them agree with the observed
increase in the Curie temperature but propose slightly varying models to account for the observed increase. It should be clearly indicated here that there exists no proof for any of the models to account for variation in $T_c$ of $\text{LiNbO}_3$ with doping. The variation in the Curie temperature in the study of Hu et al. (1991A) is shown in Figure 18. The observed variation is explained similar to the explanation by Gallagher et al. of the variation in titanium doped lithium niobate. The solid line in Figure 18 connects the actual Curie temperature in MgO doped samples as determined by a DTA. The dashed lines are calculated from the model proposed by Gallagher correlating the cation vacancy concentration and $T_c$. The points A corresponds to the MgO concentration up to which the $T_c$ increases and the point B to the composition at which the $T_c$ begins to decrease.

In the early stages of doping with MgO according to Hu et al. (1991), magnesium ions replace niobium on the lithium sites. The replaced niobium ions occupy the vacancies at the niobium sites. Although no reaction for MgO doping is given in any of the published papers, the mechanism of magnesium substitution can be expressed as:

$$\text{MgO} + V_{\text{Nb}}^{5-} + Nb^{4+}_{\text{Li}} \leftrightarrow \text{Mg}^{2+}_{\text{Li}} + Nb_{\text{Nb}}^{5+} + O^{2-}_0$$

The above reaction qualitatively leads to a decrease in the concentration of cation vacancies but there is no mechanism for charge compensation in the reaction. None of the arguments found in the literature either for the creation or annihilation of vacancies in $\text{LiNbO}_3$ have been experimentally verified and at best are hypothesis. After the niobium site vacancies are exhausted, further incorporation of magnesium results in creation of
Figure 18. The variation in the Curie temperature of LiNbO₃ with MgO doping [Hu et al. (1991A)].
vacancies and a decrease in the Curie temperature. According to Hu et al. (1991A) the rate of creation of vacancies would be dependent on the site at which the vacancies are created. It was concluded from the rate of decrease of $T_c$ beyond the 10% doping level that vacancies are created at the lithium site and magnesium is incorporated on the lithium site.

It was also observed that the distribution coefficient of MgO between the melt and the crystal [Hu et al. (1991A)] shows a change from 1.2 to 0.95 at about 5% doping level. Many of the properties of MgO doped lithium niobate show a break in behavior at about the 5-7% substitution level. This threshold is attributed to all the antisite niobium sites having been filled in the LiNbO$_3$ lattice.

The only study on powders of MgO doped lithium niobate [Katsumuta et al. (1994)] agrees with the increase in $T_c$ with MgO doping but explains it on the basis of a lithium vacancy model rather than more widely accepted Abrahams and Marsh model. This study also shows a decrease in the lattice parameter with MgO doping up to 3% and then shows an increase. This difference might arise due to the Li/Nb ratio remaining constant compared to the single crystal studies.

A number of other dopants have also been studied. If the cation vacancy model holds true, substitution by any divalent ion should lead to an increase in the Curie temperature and a decrease with tetravalent doping. It has been observed that the zinc substituted lithium niobate shows a decrease in the Curie temperature [Kawakami et al. (1986)].
Figure 19 shows the results of the study by Kawakami et al. on the ZnO system. The endo and exo in the plot refers to observations during the heating and cooling cycles respectively. A lithium vacancy model is used to explain zinc substitution in lithium niobate. Substitution of zinc at the lithium site results in the creation of additional vacancies but the decrease in Curie temperature is explained based on the decrease in c/a ratio with addition of zinc.

Although figure 19 does not show a decrease in c/a with zinc doping, the decrease in $T_c$ was attributed to the decrease in c/a [Kawakami et al. (1986)]. It is hard to arrive at a unified model for the effect of dopants on the Curie temperature as long there are discrepancies for the defect structure of the starting LiNbO$_3$ and difficulties persist in determining the actual composition of the crystal. The difficulty of identifying the dopant sites adds to the problem of arriving at a unified model for the role of dopants in controlling the $T_c$.

There has been a lot more comprehensive work on the role of dopants in LiTaO$_3$. As previously mentioned LiTaO$_3$ and LiNbO$_3$ have identical structure and show similarity in any of the physical properties. Torii et al. (1983) carried out extensive studies on lithium tantalate powders doped with various divalent oxides. It is seen from Figure 20, that the Curie temperature for divalent oxides NiO and MgO increases, while addition of ZnO and CaO decreases the Curie temperature. The effect of the dopant on Curie temperature was correlated to the change in c/a ratio with doping.
Figure 19. The variation in the lattice parameter and the Tc of LiNbO3 with ZnO doping. [Kawakami et al. (1986)].
Figure 20. The variation in the $T_c$ of LiTaO$_3$, doped with divalent oxides [Torii et al. (1983)].
It is seen from figures 20 and 21 that the dopants that cause an increase in c/a also result in an increase in $T_c$. Kawakami et al. (1985) have found a similar dependence of $T_c$ on c/a during the doping of LiTaO$_3$ with WO$_3$. These conclusions are in conflict with the cation vacancy model of Gallagher et al. (1988). If the cation vacancy model is true, doping by any divalent ion should cause an identical change in the $T_c$ of LiTaO$_3$.

One factor that is not taken into account in all these studies is the site swapping of the dopant ions between the lithium and niobium site. As the two cation sites are identical in terms of symmetry, swapping of the dopant ions between the lithium site and the niobium will become important at high temperatures [Birnie and Catchen (1993B)]. The chemical reaction that represents the equilibrium condition for dopant distribution between the sites is given by

$$I_{\text{Li}} + V_{\text{Nb}} \leftrightarrow I_{\text{Nb}} + V_{\text{Li}}$$  \hspace{1cm} (2.15)

Site swapping of impurities has been found to occur extensively in LiNbO$_3$ and experimental evidence for this phenomenon will be presented in the next section.

### 2.8 SITE OCCUPANCY OF DOPANTS IN LiNbO$_3$

There is very little conclusive evidence on the impurity site substitution in the host lattice. Many of the studies give the local site symmetry. In many of the crystal systems,
Figure 21. The variation in the lattice parameter and c/a ratio of LiTaO₃, doped with divalent oxides [Torii et al. (1983)].

X=Dopant Concentration
local site symmetry information is enough to pinpoint the site of the dopants. In the case of lithium niobate all of the available sites for impurity atoms have octahedral symmetry and so many of the spectroscopic techniques cannot give sufficient information about the site occupancy of the dopants. Recently there have been renewed attempts to identify the site of dopant ions in lithium niobate. Ion beam methods, extended x-ray absorption fine structure (EXAFS), electron paramagnetic resonance (EPR), electron double resonance and perturbed angle spectroscopy (PAC) are some of the methods that are being used to investigate the dopant site in lithium niobate. Computer simulation also has been used to determine site occupancy of dopants [Donnenberg (1991)]. The results of such studies will be briefly summarized.

2.8.1 Computer Simulation

Calculations based on the shell model discussed previously were again used to investigate the role of defects in lithium niobate. One of the assumptions was, that the impurity dissolution was independent of the pre-existing intrinsic defect structure. This assumption sidesteps the issue of the defect structure of congruent lithium niobate. A number of solution reactions are possible for the dissolution of divalent ions in LiNbO$_3$ and few of them are given below. Some of the reactions do not meet the conditions required for charge and site balance.
Equation (2.16d) represents the self compensation mechanism, where the dopants occupy both Li and Nb sites in such a ratio so as to maintain charge neutrality. Table 5 summarizes the results for the energy of solution for impurity ions incorporated into LiNbO₃ from computer model calculations.

It is evident that self-compensation is the favored mechanism for dopant incorporation into LiNbO₃. But in this model intrinsically pre-existent defects are not taken into account.
Table 5. Energy for incorporation of dopant ions into LiNbO₃

<table>
<thead>
<tr>
<th>Impurity ion</th>
<th>Site of incorporation</th>
<th>Favored intrinsic charge compensator Solution energy (eV) per impurity ion</th>
<th>Solution energy (eV) per impurity ion for self-compensation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺</td>
<td>Li, Nb</td>
<td>Li⁴⁻&lt;sub&gt;Nb&lt;/sub&gt; 8.1, V₂⁺&lt;sub&gt;O&lt;/sub&gt; 9.5</td>
<td>7.3</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>Li, Nb</td>
<td>Li⁴⁻&lt;sub&gt;Nb&lt;/sub&gt; 9.4, V₂⁺&lt;sub&gt;O&lt;/sub&gt; 8.3</td>
<td>7.3</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>Li, Nb</td>
<td>Li⁴⁻&lt;sub&gt;Nb&lt;/sub&gt; 7.4, V₂⁺&lt;sub&gt;O&lt;/sub&gt; 8.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Mn³⁺</td>
<td>Li, Nb</td>
<td>Li⁴⁻&lt;sub&gt;Nb&lt;/sub&gt; 13.8, V₂⁺&lt;sub&gt;O&lt;/sub&gt; 12.6</td>
<td>11.7</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>Li, Nb</td>
<td>Li⁴⁻&lt;sub&gt;Nb&lt;/sub&gt; 8.5, V₂⁺&lt;sub&gt;O&lt;/sub&gt; 9.9</td>
<td>7.7</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>Li, Nb</td>
<td>Li⁴⁻&lt;sub&gt;Nb&lt;/sub&gt; 9.2, V₂⁺&lt;sub&gt;O&lt;/sub&gt; 10.6</td>
<td>8.4</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Li, Nb</td>
<td>Li⁴⁻&lt;sub&gt;Nb&lt;/sub&gt; 2.7, V₂⁺&lt;sub&gt;O&lt;/sub&gt; 5.1</td>
<td>2.2</td>
</tr>
<tr>
<td>Ti⁴⁺</td>
<td>Li, Nb</td>
<td>Li⁴⁻&lt;sub&gt;Nb&lt;/sub&gt; 15.2, V₂⁺&lt;sub&gt;O&lt;/sub&gt; 12.1</td>
<td>11.7</td>
</tr>
</tbody>
</table>
If the intrinsic defect present in LiNbO₃ is taken into account the energetics of the reaction

\[ M^3_{\text{Nb}} + \text{Nb}^4_{\text{Li}} \rightleftharpoons M^1_{\text{Li}} + \text{Nb}_{\text{Nb}} \]  

control the site occupancy of the dopants. In the case of Ti⁴⁺, if a defect complex of the type (Nb_{Li}⁴⁺V_{Nb}⁻) is considered, Nb site incorporation is favored. If isolated Nb^4_{Li} is considered as the intrinsic defect, then Ti⁴⁺ ions are seen to be incorporated in the Li site [Schirmer et al. (1991)]. Thus at present there is no certain decision concerning the titanium occupancy in LiNbO₃.

### 2.8.2 EXAFS

EXAFS probes local structure around the cation and provides information about the sites occupied by the cation [Bush et al. (1992)]. There would be a large dissimilarity of the cation shells around the dopant depending on whether the dopant occupies lithium or niobium sites. If the dopant occupies lithium sites, then the shell will contain Nb ions which are strong backscatterers of photoelectron waves. On the contrary, if the dopant occupies niobium sites, the shell will contain lithium ions which are weak back scatterers of photoelectrons.

Hafnium and tantalum doped samples were the first samples to be studied using EXAFS [Prieto et al. (1991)]. Based on that study it was proposed that Hf⁴⁺ occupies lithium
sites while Ta$^{5+}$ occupies niobium sites. Tantalum occupancy of niobium sites is not surprising because of the isomorphous structure of LiNbO$_3$ and LiTaO$_3$. The occupancy of lithium site by Hf$^{4+}$ is a little surprising. As the values for the ionic radii of Li$^{1+}$ (0.68 Å) and Nb$^{5+}$ (0.69 Å) are very similar, it was expected that only the difference in charge would influence the site occupancy of the dopants. From a charge compensation criterion Hf$^{4+}$ would be expected to occupy Nb$^{5+}$ sites. In this study also no mechanism is given for charge compensation.

Preliminary work has been done on the site occupancy of Ti$^{4+}$ in LiNbO$_3$. Zaldo et al. (1991) have grown lithium niobate single crystals from a melt of congruent composition with 1% titania. The titanium was found to occupy lithium sites. It has been proposed that all dopants occupy lithium sites in small concentration and would occupy niobium sites only after antisite niobiums have been removed. This study was done with a very low concentration of titanium ions and it is far removed from the situation under which waveguides in lithium niobate are formed.

Study of cobalt doped lithium niobate [Chadwick (1993)] also shows the existence of cobalt on the lithium sites. As all of this work has focused on identifying the dopant sites, none of them have proposed any charge compensating mechanism for the incorporation of dopants in the host lattice. At best, these works are in their early stages and much more work has to be done before arriving at a comprehensive dopant incorporation mechanism.
2.8.3 Optical Methods

Sole et al. (1993) have used optical methods (absorption and site selective fluorescence) to detect impurity sites in lithium niobate. This study was done using very small concentrations (0.1 to 1%) of rare earth and transition metal ions. Figure 22 shows the absorption as a function of wavelength for Eu$^{3+}$ and Cr$^{3+}$ doped lithium niobate. It was concluded from this study that all trivalent ions studied occupied both lithium and niobium studies. This result is in conflict with the EXAFS results discussed in the previous section.

2.8.4 Perturbed Angular Correlation (PAC)

The PAC technique probes the interaction between nuclear quadrupole moment of a suitable nucleus and the electric field gradient produced by surrounding electric charges. [Hauer et al. (1994)]. PAC measures hyperfine interactions at the site of the radioactive probe atoms that are substituted in well-defined lattice sites in the crystal [Birmie et al. (1993A)]. The γ-γ PAC technique probes the interaction between the nuclear quadrupole moment of a suitable nucleus and the electric field gradient produced by the surrounding ions in a crystal lattice. Deviations from perfect symmetry in the nearest neighbors lead to large effects and thus this technique is suitable for determining the site occupancy of the dopants. In the last three years the PAC technique has been used to probe site occupancy of LiNbO$_3$ [Catchen et al. (1992)]. A $^{181}$Hf to $^{181}$Ta probe has been used to investigate the role of dopants in LiNbO$_3$. As the chemistry of Hf$^{4+}$ ions is similar to
Figure 22. A spectral region in the optical absorption spectrum of congruent LiNbO₃ doped with chromium and europium. The spectroscopic transition for Cr³⁺ corresponds to the \( ^4A_2 \rightarrow E^\circ(E) \) transition [Sole et al. (1993)].
that of Ti$^{4+}$ ions and nearly identical to Zr$^{5+}$ ions, the Hf$^{4+}$ probe is well suited for study in LiNbO$_3$. Catchen et al (1992) have specifically studied the partitioning of $^{181}$Hf between the lithium and niobium site as a function of temperature. At temperatures below 1100 K and at concentrations of about 0.03%, $^{181}$Hf substitutes primarily into the Li sites. At higher temperatures, the Hf$^{4+}$ ion transports between lithium site and the niobium site. There is a strong temperature dependence of the site occupancy of Hf$^{4+}$ ion. Figure 23 shows the site occupancy dependence of the Hf$^{4+}$ probe as a function of temperature. Thus at temperatures close to the Curie transition Hf$^{4+}$ ions can occupy both sites and defect models derived from cation vacancy concentration at room temperature will not be applicable at high temperatures. PAC measurement using $^{44}$Ti shows the Ti to occupy Li sites [Hauer (1994)]. These studies are in conflict with previous findings of Ti$^{4+}$ ions on niobium sites. The application of PAC to lithium niobate is in its rudimentary stage and more comprehensive work can be expected in the near future.

It is seen from the above discussion, experimental methods to determine the site occupancy of the dopants are in the developmental stages and does not give a complete picture of the site occupancy of the defect and the charge compensating defects. The different types of possible defects that can occur in this system and the low concentrations in which these defect occur make it difficult to develop a self-consistent model.
Figure 23. The log dependence of the site occupancy ratio $A_1/A_2$ on the inverse temperature for LiNbO$_3$. $A_1$ is the occupancy of the niobium site and $A_2$ the lithium site [Dunbar and Catchen (1993B)].
2.9 FERROELECTRIC TRANSITION IN LiNbO$_3$

In order to understand the role of dopants in controlling the Curie transition temperature an understanding of the mechanism of transition in lithium niobate is needed. As might be expected from the previous discussion there are various theories about the mechanism ferroelectric (FE) to paraelectric (PE) transition in lithium niobate. The study of the ferroelectric transition in LiNbO$_3$ by x-ray diffraction is difficult because of the high temperature of transition and volatility of lithium. Thus there is very little direct work done in measuring the atomic position of LiNbO$_3$ in the paraelectric phase.

Figure 24 shows the two possible mechanisms by which the FE to PE transformation can occur in LiNbO$_3$ [Dunbar (1991)]. The solid lines in the picture represent oxygen layers. The picture on the left shows the arrangement of the cations in the ferroelectric state of lithium niobate. In the figure on the left, the niobium and lithium ions are off-center. This displacement of the lithium ion and the niobium ion leads to ferroelectricity in LiNbO$_3$. The displacement model (Figure 24, middle) shows all the lithium atoms moving gradually towards the center of the oxygen layer that separates the lithium site and the normally vacant octahedral site. The niobium ion moves to the center between two oxygen planes. When the lithium atom is in the center, the spontaneous polarization will reach zero signifying transformation to the PE phase. The disordering model (Figure 24, right) proposes that there is an equal distribution of lithium atoms between the vacant octahedral site and the regular site. The position of niobium ions in both the models are identical.
Figure 24. The arrangement of cations in LiNbO$_3$ [Dunbar (1991)]. (Left. Ferroelectric state, Middle - Paraelectric state according to the displacement model, Right - Paraelectric state according to the disordering model. The half circles represent 50% probability of occupation at this site).
Early neutron spectroscopic studies seemed to suggest a displacive transformation. More recent work done using Raman spectroscopy [Raman and Ballman (1986)] supports the order-disorder model for this transformation. Support for the disordering model also arises from work on lithium tantalate. As lithium tantalate has a lower Curie transition temperature, XRD has been used to study the ferroelectric transformation and these studies support an order-disorder type transition. [Abrahams et al. (1973)].

The defect reaction that describes the order-disorder aspect of the transition is

\[ \text{Li}_{\text{Li}} \leftrightarrow \text{V}_{\text{Li}} + \text{Li}^0_{\text{i}} \] (2.18)

This reaction progresses until the two possible crystal structural stacking sequences

\[ \text{Nb, Li, V, Nb, Li, V} \] (2.19a)

\[ \text{Nb, V, Li, Nb, V, Li} \] (2.19b)

are no longer distinguishable. When the lithium atom becomes evenly distributed between the two arrangements, the two arrangements become identical and correspond to the ferroelectric to the paraelectric transition. The presence of niobium or dopants on the lithium site requires these ions also be equally disordered between the two sites.
Dunbar (1991) has developed a thermodynamic model based on a calculation of the enthalpy from dipole-dipole interaction and configuration entropy to explain the ferroelectric transition in LiNbO$_3$.

The Curie temperature was determined to vary with the lithium vacancy concentration as

$$T_c = T_c^0 [1 - V (3/8 + B^2/8)]$$  \hspace{1cm} (2.20)

where $T_c^0$ is the Curie temperature when the vacancy concentration (V) is 0 and B is an empirical constant derived from the slope of the Curie temperature and vacancy concentration. Tomov et al. (1989) have studied the ferroelectric transition in Fe-doped LiNbO$_3$ using Mossbauer spectroscopy and have found evidence for the order-disorder type transition. The order-disorder transformation is currently accepted as the mechanism for the ferroelectric transformation in lithium niobate.

2.10 NEUTRON DIFFRACTION

The thermal neutron, an uncharged and weakly interacting particle, is a versatile probe for the study of solids and liquids [Yelon (1990)]. Neutrons exhibit wave properties, with a wavelength $\lambda$ at room temperature of about 1.5\AA. This value is on the order of an interatomic distance and very close to the wavelength of copper $K_\alpha$ (1.54 \AA) used in X-ray diffraction studies [Bacon (1963)]. Thus the neutrons should show good diffraction
effects when they interact with a crystal and this enables neutrons to be used in
diffraction studies.

When a beam of neutrons interact with the assembly of atoms, it is the nuclei of the
atoms that are effective in scattering the neutron beams. The extent of this scattering is
measured by the cross section of the nucleus and increases slowly with the atomic weight
of the atom. Superimposed on this effect due to the size of the nucleus is a process
known as “resonance” scattering. The incident neutron and the target nucleus combine
to form a “compound nucleus”. Resonance scattering is a function of the energy levels of
this compound nucleus and this resonance scattering is superimposed on the ordinary
scattering due to the nuclear size. As a result of this superimposition, the extent to which
the atoms scatter neutrons does not vary uniformly across the periodic table.

Thus the unusual feature of neutron diffraction is that the coherent scattering $\sigma_{\text{coh}}$ and
the quantity $b = 4\pi\sigma_{\text{coh}}$, that relate neutron-nuclear interaction, show wide variation from
one species to another. In the case of x-rays, the cross section for scattering is
proportional to the number of electrons and so light elements and elements close to each
other in the periodic table are difficult to distinguish. In the case of neutron scattering
$\sigma_{\text{coh}}$ is not a function of the atomic number. Table 6 shows the value of $\sigma_{\text{coh}}$ for some
elements [Yelon (1990)]. Thus light elements contribute significantly to scattering and
adjacent elements can be distinguished using neutron diffraction. The table also shows
that even isotopic substitution can change the scattering without affecting the physical
and chemical nature of the system. The absorption cross section, $\sigma_a$, is small for most of
the elements and the beam will penetrate millimeters into samples. This enables large samples to be studied. The reader is referred to two excellent books by G. E. Bacon (1963, 1966) for further details on neutron diffraction.

Lithium niobate is an ideal candidate for study with neutron diffraction. Lithium being a light element is not very amenable for study by x-ray diffraction. It can be seen from table that the scattering length for lithium \((-0.190\times10^{-12}\text{ cm})\) and Nb \((0.754\times10^{-12}\text{ cm})\) are very different and have opposite magnitudes. Thus a neutron scattering experiment can give information about the site occupancy of lithium and niobium in the lattice. In contrast, lithium being light does not scatter X-rays.

There is only one previous report on the study of LiNbO₃ using neutron diffraction [Iyi et al. (1992)]. Neutron diffraction study on powdered samples has been expanded due to the availability of Rietveld refinement method. The profile refinement procedure developed by Rietveld (1969) compensates for the loss of information arising from the powdered samples. One reason for the lack of extensive neutron diffraction study is the lack of availability of neutron sources. A nuclear reactor is generally required to act as a source of neutrons and this severely restricts availability. Neutron diffraction has been used in this study to probe defect structure and site occupancy of dopants.
2.11 PURPOSE AND SCOPE OF THIS STUDY

The formation of waveguides in titanium doped lithium niobate was discussed previously. Titanium doped lithium niobate waveguides suffer from the following drawbacks.

(1) The starting material for the formation of a titania doped waveguide is a single crystal lithium niobate grown from the congruent composition. The crystal grown from the congruent composition is cooled in the presence of an electric field to form a single domain structure. This single domain structure ensures minimum optical loss. If this single domain crystal is taken to a temperature above its Curie temperature multi-domain crystals are formed. Thus in order to maintain the quality of transmission, further processing of lithium niobate should be done below its Curie temperature.

The formation of a waveguide involves depositing titanium on the single domain LiNbO₃ and a subsequent diffusion step. In order to achieve satisfactory rates of diffusion the temperature of diffusion should be above 1000°C. It was pointed out in an earlier section that the Tᵥ falls below 1000°C on doping with titania. The diffusion anneal destroys the single domain structure that had been manufactured with great care. Thus the decrease in the Curie temperature in essence is one of the biggest problems in the production of titania doped waveguides.

(2) In order to minimize the above mentioned problem, the temperature of diffusion of titanium into LiNbO₃ is kept below 1000°C. This low temperature of diffusion prevents
satisfactory diffusion of titanium into $\text{LiNbO}_3$ and as a result well-defined channel waveguides are not formed.

(3) The ‘a’ and ‘c’ lattice parameters decrease non-uniformly on doping with titania. This introduces non-uniform strains in the crystal and a subsequent drift in the device performance during application.

(4) During the long times needed for the diffusion of titanium into lithium niobate there is significant out-diffusion of lithium from the crystal. This out-diffusion of lithium modifies the refractive index of lithium niobate and alters the quality of transmission.

(5) Lithium niobate suffers from photorefractive damage, the susceptibility to laser radiation. The laser radiation itself alters the refractive index of $\text{LiNbO}_3$ and affects the quality of transmission.

The goal of this study was to extensively investigate the effect of doping $\text{LiNbO}_3$ with magnesium titanate. Some of the present theories correlate the $T_c$ to the cation vacancy concentration and the $c/a$ ratio. As $\text{LiNbO}_3$ and $\text{MgTiO}_3$ have the same cation to the anion ratio, doping should not change the cation vacancy concentration and hence the Curie temperature. If the $T_c$ can be maintained, problems 1 and 2 mentioned above can be solved. In addition doping $\text{LiNbO}_3$ with MgO has been found to minimize problems 3 and 4 [Bryan et al. (1985)]. Thus it is expected that doping $\text{LiNbO}_3$ with $\text{MgTiO}_3$ would solve most of the disadvantages associated with the titania system.

In addition to these specific problems with the titania doped lithium niobate, some of the other problems associated with this system are:
(1) Defects introduced in congruent lithium niobate to account for the deficiency of lithium has not been established;

(2) There have been a number of models proposed to explain the relationship between the dopant concentration and the $T_c$. These models have been proposed after study on one or two specific systems but the applicability of the models have not been tested extensively;

(3) Solid solubility information of only TiO$_2$ and MgO in LiNbO$_3$ is available. Solid solubility information of other dopants in LiNbO$_3$ would facilitate further research on the LiNbO$_3$ system.

(4) There have been very few attempts to study the site occupancy of dopants in lithium niobate. Although titanium doped LiNbO$_3$ has been used for over twenty years, the site occupancy of titanium in LiNbO$_3$ has still not been unequivocally established.

In this research in addition to the investigation of LiNbO$_3$ - MgTiO$_3$ system, the solid solubility of various dopants in LiNbO$_3$ were determined. The change in the Curie temperature of lithium niobate with the addition of several dopants were determined and the applicability of the various models to explain the variation in the Curie temperature were tested. Attempts were made to use neutron diffraction to gain insights into the defect structure of lithium niobate and the site occupancy of dopants in lithium niobate. The suitability of neutron diffraction as a tool in the study of LiNbO$_3$ was also evaluated.
CHAPTER III
EXPERIMENTAL PROCEDURE

3.1 PROCESSING

3.1.1 Processing of Lithium Niobate

Lithium niobate was made by solid state reaction between lithium carbonate (Johnson Mathey, JM) and Nb$_2$O$_5$ (JM). Thermogravimetric analyses (TGA) of the starting powders were done using a Perkin-Elmer System 7 TGA, to determine the moisture content of the starting powders. As an example, Figure 25 shows the TGA curve for MgCO$_3$.XH$_2$O. The TGA curve shows a two-step loss in weight. The initial loss corresponds to the loss of water and the subsequent loss to the decomposition of MgCO$_3$ to MgO. The value of X was determined in this manner.

The lithium carbonate and niobium oxide powders were thoroughly mixed in the proper ratio using a mortar and pestle. The powders were not ball milled to avoid contamination from the milling medium. The powders after mixing were calcined in a platinum crucible. The crucible was covered and encapsulated in powders of same composition to avoid loss of lithium. The powders were fired in a box furnace to 1100°C at a heating rate of 10°C/min. and held for six hours. After cooling, the powders were crushed and
Figure 25. Results from the TGA on the powders of MgCO$_3$.XH$_2$O
fired again to 1150° C for six hours. The powders were then characterized and used for doping with other oxides. Lithium niobate powders that had been processed in-house were used for preliminary work. Since the concentration of lithium, as measured by the Curie temperature, changed from batch to batch, commercial LiNbO₃ (JM) was used in the later stages of the project. The use of commercial powder ensures the starting composition of LiNbO₃ was maintained.

3.1.2 Processing of doped powders

The steps involved in the processing of doped LiNbO₃ powders were identical to the steps in the processing of pure LiNbO₃ powders. The various dopants studied and the compositions studied are shown in Table 7.

Table 7. Dopants and concentration studied in LiNbO₃.

<table>
<thead>
<tr>
<th>DOPANT</th>
<th>CONCENTRATION (Mole %)</th>
</tr>
</thead>
<tbody>
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<td>Magnesium Titanate (MgTiO₃)</td>
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</tr>
<tr>
<td>Titanium dioxide (TiO₂)</td>
<td>5, 10, 15</td>
</tr>
<tr>
<td>Magnesium Oxide (MgO)</td>
<td>5, 10, 15</td>
</tr>
<tr>
<td>Zinc Oxide (ZnO)</td>
<td>5, 10, 15, 25</td>
</tr>
<tr>
<td>Calcium Oxide (CaO)</td>
<td>5, 10, 15</td>
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<tr>
<td>Nickel Oxide (NiO)</td>
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</tr>
<tr>
<td>Zirconium Oxide (ZrO₂)</td>
<td>5, 10</td>
</tr>
<tr>
<td>Vanadium Oxide (V₂O₅)</td>
<td>5, 10</td>
</tr>
</tbody>
</table>
3.2 CHARACTERIZATION

3.2.1 X-ray Diffraction

Careful x-ray diffraction work was carried out to identify the phases present and also to calculate the lattice parameters. The diffraction patterns were obtained using a "Scintag Pad V" x-ray diffractometer. Copper $K_\alpha$ radiation (wavelength 1.5406 Å) generated using a 45KV and 20mA source was used. The XRD data were collected under two different modes. For phase identification and measurement of the lattice parameter, the diffraction patterns were collected in the continuous mode at a scan rate of 0.5°/minute and at a step size of 0.03. The data were collected for 2θ values between 15° and 119° and a typical run took about four hours. In order to detect second phases diffraction was also done in the step scanning mode. In the step scanning mode of data collection, data are collected until either a preset count or a preset time is reached. This mode of data collection increases the signal/noise ratio and enables minor phases to be identified. The preset count was set at 200 while the preset time used was 20 seconds.

Silicon was used as the internal standard to correct for peak shifting in the calculation of lattice parameters. The JCPDS card for silicon is reproduced in Appendix B. Silicon peaks between 20-120° were used to correct for any shift in the position of the peaks. The silicon peak at 56.141° was neglected as a peak of LiNbO$_3$ occurs very close to this angle. A third order polynomial was used to fit the shift in the position of peaks of silicon. The positions of peaks in the processed powders were then corrected using this third order polynomial.
The lattice parameters were calculated using a least square fitting program. A search match program supplied by the manufacturer was used to identify the second phases present on doping lithium niobate. In order to identify the phases, the minimum number of peaks required to identify a phase and the Δd value within which the peak should occur were varied.

3.2.2 Neutron Diffraction

Neutron diffraction was done with the help of Prof. W. Yelon and Dr. Z. Hu at the Univ. of Missouri Research Reactor Center. The neutron diffraction data were collected using a position sensitive detector (PSD). The PSD diffractometer is a high resolution instrument of non-conventional design and the resolution is approximately $2\times10^{-3}$ $(\delta\lambda/\lambda)$ [Z. Hu (1994)]. The total normal intensity ($I_0$) has contributions from nearby reflectors and from background scattering. The contributions from reflections are calculated from the structure factors. About 2 grams of the powdered samples were encased in a vanadium can having a 3mm diameter for the diffraction study.

In structural analysis using neutron diffraction, the diffraction pattern is collected and then a theoretical pattern is developed for comparison. The theoretical pattern is developed from a knowledge of the space group, thermal parameter, background function, neutron scattering factor and the wavelength of the neutron used. Parameters that are refined include cell parameters, atomic positions and the occupancy at each site. The quality of the agreement between the observed and calculated profiles is measured by
a set of conventional factors: Profile R-factor $R_p$, weighted profile R-factor $R_{wp}$, expected R-factor $R_{exp}$ and $\chi^2$.

$$R_p = \frac{\sum (Y_i(obs) - Y_i(calc))}{\sum Y_i(obs)} \quad (3.1)$$

$$R_{wp} = \left[ \frac{\left\{ \sum Y_i(obs) - Y_i(calc) \right\}^2}{\sum W_i Y_i(obs)^2} \right]^{1/2} \quad (3.2)$$

$$R_{exp} = \left[ \frac{\left( N - P + C \right)}{\sum W_i Y_i(obs)^2} \right]^{1/2} \quad (3.3)$$

where $N$ is the number of observations or points in the pattern, $P$ is the number of refined parameters, $C$ is the number of constraints and $N-P+C$ is the total number of free parameters in the Rietveld refinement [Hu (1994)]. $Y_i$ in the above equation refers to the structure factor.

$$\chi^2 = \left( \frac{R_{wp}}{R_{exp}} \right)^2 \quad (3.4)$$

The quantity $\chi^2$ is defined as the ratio between the weighted profile R-factor and the expected R-factor. The goal of refinement is to minimize $\chi^2$. 
3.2.3 Determination of the Curie Temperature

The Curie transition temperatures were determined using a Perkin-Elmer DTA1700 and an optical DTA. Details about the principle of operation and construction of the optical DTA are given in Appendix 1. The PE DTA is a computer controlled heat-flux calorimeter. The temperatures of the sample and the reference are measured using a matched pair of types thermocouples, Pt-Pt/10%Rh. The difference in temperature between the sample and the reference gives the $\Delta T$ value.

Pure $\alpha$-alumina supplied by PE is used as the reference material and high purity gold (JM, 99.999%) is used as the standard to calibrate the DTA. Data are collected at a heating rate of 20° C/min. in flowing oxygen. Typically about 100 mg of the sample in a platinum crucible were used to determine the $T_c$. After data acquisition software supplied by the manufacturer is used for determination of the $T_c$ and further analysis.

3.2.4 Microscopy

Scanning electron microscopy and energy dispersive spectroscopy were done to determine the particle size and distribution of dopants in lithium niobate. The powders were deagglomerated in an ultrasonic bath before being mounted on an aluminum substrate. The powders were sputter-coated with gold and then observed using a Hitachi SEM operating at 25KV in the secondary electron image mode.
3.2.5 Refractive Index Measurement

In-house attempts to measure the refractive index change failed because of the large value of refractive index and the birefringent nature of LiNbO$_3$. The liquids required to make the refractive index measurement were very expensive and a petrographic microscope is required due to the birefringent nature of LiNbO$_3$.

Measurement of the refractive index for starting lithium niobate and LiNbO$_3$ doped with 5% magnesium titanate were done at the R. P. Cargille laboratories Inc. NJ, using the Becke line method. In this method a solid of unknown refractive index is immersed in a liquid of known refractive index. When the focus of the microscope is raised, a line of light, the Becke line, will go into the medium of the higher refractive index, either the solid or the liquid. This process is repeated with liquids of incremental refractive index (Cargille Refractive Index Liquids and Melts) until the refractive index of the solid is found to be between two liquids or equal to a liquid of known refractive index. The birefringent nature of LiNbO$_3$ requires that the powders be properly oriented before using the Becke line technique [R. Sacher (1994)]. The right orientation is achieved using a petrographic microscope with a revolving stage and two polarizers: one below the specimen and one above the specimen. Using crossed polarizers the stage is rotated until the image of the crystal reaches extinction. At this point the upper polarizer is removed and the refractive index in one direction is measured. The upper polarizer is replaced and the stage is rotated 90° to a second extinction and the second refractive index of the crystal is measured. The measurements of refractive index were made at 25° C using light of wavelength 5893 Å.
CHAPTER IV
RESULTS AND DISCUSSION

4.1. LITHIUM NIOBATE

Processing LiNbO$_3$ was performed using different temperature profiles and it was observed that calcining at 1100°C and 1150°C for six hours produced satisfactory powders. All the peaks in the x-ray diffraction pattern of the powders were indexed and matched with JCPDS standard for LiNbO$_3$. X-ray diffraction pattern of single phase LiNbO$_3$ is shown in Figure 26 and the corresponding JCPDS card used to index the pattern is reproduced in Appendix B. The diffraction pattern of commercial LiNbO$_3$ confirmed the presence of single phase LiNbO$_3$ within the limits of detection by x-ray diffraction. The detectability limit of x-ray diffraction was determined by preparing physical mixtures of LiNbO$_3$ and MgTiO$_3$. X-ray diffraction was done on the physical mixtures and the pattern was analyzed for peaks of the minor phase. The detectability limit of x-ray diffraction was determined to be about 3% based on this approach. All the peaks in the x-ray diffraction pattern are indexed and the procedure used to calculate lattice parameters is outlined in Table 8.
Figure 26. XRD pattern of the initial (undoped) lithium niobate powder.
Table 8. Method for the calculation of lattice parameters.

The d-spacing for a hexagonal system is given by:

\[
\frac{1}{d^2} = 4(h^2 + hk + k^2)/(3a^2) + \frac{1}{c^2}
\]  

(4.1)

The following quantities are defined:

\[D = \frac{1}{d^2}, \quad A = \frac{1}{a^2}, \quad C = \frac{1}{c^2}, \quad r = \frac{4}{3}(h^2 + hk + k^2)\]  and \[s = \frac{1}{c^2}\]

Equation 4.1 can now be written as a linear equation in two variables and can be written as

\[D = rA + sC\]  

(4.2)

An equation similar to 4.2 can be written for each of the indexed planes in the XRD pattern.

The "normal" equations for the least square solution of the linear equation are the following:

\[
\sum r_i^2 A + \sum r_i s_i C = \sum r_i D_i
\]  

(4.3)

\[
\sum s_i^2 C + \sum r_i s_i A = \sum S_i D_i
\]  

(4.4)

Solution of equations 4.3 and 4.4 yield A and C from which the lattice parameters a and c are calculated [Cullity (1986)].

The output of the lattice parameter program is shown in Table 9. The lattice parameters of commercial LiNbO₃ were calculated to be \[a_h = 5.1573\text{Å} \quad (0.0004)\] and \[c_h = 13.884\text{Å} \quad (0.0007)\].
The Curie temperature of the samples was determined after calibration of the DTA using a standard of gold. The melting of gold as observed in a DTA is shown in Figure 27. The observed temperature for the onset of melting is adjusted to correspond to 1064.43 °C, the recommended temperature from the Handbook of Chemistry and Physics (1989). The Perkin-Elmer program used to determine the glass transition temperature is used in the determination of $T_c$. The method of determination of $T_c$ using a DTA is shown in Figure 28. Tangents are drawn to the curve corresponding to the specific heat in the ferroelectric and the paraelectric phase and the $T_c$ corresponds to the temperature at which $C_p = \Delta C_p/2$.

Figure 29 shows the Curie transition in LiNbO$_3$. The Curie transition temperature for the samples prepared in-house were determined to be $1139 \pm 2^\circ$C. The $T_c$ for the commercial LiNbO$_3$ was determined to be $1143 \pm 1^\circ$C for six runs of the sample. The literature value of $T_c$ for LiNbO$_3$ of congruent composition varies between 1130°C [Gallagher (1985)] and 1140°C [Kawakami et al. (1986)]. This slightly larger value of the $T_c$ indicates that the composition of the commercial LiNbO$_3$, is richer in lithium than the congruent composition. The larger lattice parameter values also indicate a lithium excess compared to the congruent LiNbO$_3$. The in-house prepared samples as they are prepared carefully and in small quantities are closer to the congruent composition than the commercial samples.

The $T_c$ in addition to being a function of lithium concentration also depends on the method of measurement. Measurement of $T_c$ using DTA is done with no alternating
Table 9. Sample output of the lattice parameter calculation program.

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<th>CALC</th>
<th>DELTA</th>
<th>D - SPACINGS</th>
<th>OBS</th>
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<tr>
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<td>92.0494</td>
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<td>0.93714</td>
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<td></td>
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</table>

**CELL PARAMETERS:**

\[
\begin{align*}
A &= 5.145428 \\
ESD A &= 0.000187 \\
B &= 5.145428 \\
ESD B &= 0.000187 \\
C &= 13.865781 \\
ESD C &= 0.000810 \\
\end{align*}
\]

\[
\begin{align*}
\text{ALPHA} &= 90.000 \\
\text{ESD ALPHA} &= 0.000 \\
\text{BETA} &= 90.000 \\
\text{ESD BETA} &= 0.000 \\
\text{GAMMA} &= 120.000 \\
\text{ESD GAMMA} &= 0.000 \\
\end{align*}
\]

\[
\begin{align*}
\text{VOLUME} &= 317.92
\end{align*}
\]
Figure 27. DTA plot showing the melting of gold. (calibration standard)
Figure 28. Determination of $T_c$ using the glass transition program.
Figure 29. DTA plot showing the Curie transition in the undoped lithium niobate.
field while the dielectric measurements are done in the presence of a field. The $T_c$ is influenced by the presence of the field and shows an apparent increase due to the time dependent nature of the technique. A difference of about 15°C is observed in the $T_c$ measured by the two techniques.

Table 10 shows the site occupancy of the atoms in the undoped lithium niobate for the best fit between refined structure and the observed data.

Table 10. Site Occupancy in LiNbO$_3$.

<table>
<thead>
<tr>
<th>Site</th>
<th>% Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>96.1(0.3)</td>
</tr>
<tr>
<td>Nb</td>
<td>100</td>
</tr>
<tr>
<td>O</td>
<td>99.7(1)</td>
</tr>
</tbody>
</table>

Refinements to the structure of LiNbO$_3$ were tried under different conditions. Refinements under conditions of niobium vacancies resulted in a profile very different from the observed profile. The results reported above were obtained by constraining the niobium site occupancy to be 100% and by varying the occupancy at the lithium site and the oxygen site. The value in the parentheses represents the uncertainty in the oxygen site occupancy. It is seen from Table 10 that the oxygen site is occupancy close to 100%.

Number of researchers have investigated the oxygen stoichiometry in LiNbO$_3$. Lerner et al. (1968) measured the density of LiNbO$_3$ as a function of lithium concentration. The density of LiNbO$_3$ increases on going from the stoichiometric to the congruent
composition and vacancies at the oxygen sites can not explain this observed increase in density. Abrahams and Marsh (1986) have not found any evidence for oxygen vacancies based on their combined single crystal x-ray diffraction work and measurement of density. Thus the neutron diffraction result agrees with literature reports describing complete occupancy of the anion sites.

Neutron diffraction ruled out niobium vacancies as the charge compensating defect to account for the deficiency of lithium. This does not agree with the model proposed by Abrahams and Marsh (1986). Abrahams and Marsh had proposed niobium at lithium sites and vacancies at the niobium sites to compensate for lithium deficiency. But as pointed out in the chapter on literature review, two recent publications [Iyi et al. (1992) and Wilkinson et al. (1993)] have also not found any evidence for niobium site vacancy.

The occupancy at the lithium site is about 96.1%, indicating that vacancies occur at the lithium site. One of the discrepancies in this result, is that there is no charge compensation for the defect $[V_{Li}]^{-}$. The vacancies of lithium should be charge compensated either by vacancies of oxygen or antisite defects $[Nb_{Li}]^{4+}$. As the oxygen lattice is complete, $[Nb_{Li}]^{4+}$ should be present. Our studies to date, do not show the existence of this antisite defect.

From Table 10, a simple charge balance criterion could be used to arrive at the concentration of the $[Nb_{Li}]$ site.
\[ [V_{Li}^-] = 4[Nb_{Li}^{4+}] \]
\[ [Nb_{Li}^{4+}] = \frac{3.9}{4} = 0.975 \] (4.5)

If the niobium vacancy model is true the concentration of \([Nb_{Li}^-]\) should be about 3.9%. On the other hand if the lithium vacancy model is true, the concentration of \([Nb_{Li}^-]\) should be about 0.975%. The neutron diffraction should definitely be able to detect concentrations at the 4% level. Thus the neutron diffraction results indirectly show that the lithium vacancy as the more likely charge compensating mechanism. Blumel et al. (1994) have used a similar logic to explain their NMR results. As they were unable to determine a second site for niobium, they proposed vacancies of lithium for charge compensation.

Although the focus of this study was not on the defect structure of LiNbO₃, the results of the neutron diffraction study provides further data on the defect chemistry of LiNbO₃. Although the niobium vacancy model of Abrahams and Marsh is widely accepted, there have been three publications in the last three years [Iyi et al. (1992), Wilkinson et al. (1993) and Blumel et al. (1994)], providing evidence against this model. This is the first time, evidence has been provided for the lithium vacancy model, using neutron diffraction on powdered samples.

### 4.2 MAGNESIUM TITANATE

The focus of this study was on the effect of magnesium titanate on the properties of lithium niobate. The processing conditions were optimized by experimenting with
different calcining schedules on the LiNbO₃ doped with 5% MgTiO₃. Calcining at 1100°C and 1150°C for six hours resulted in a single phase LiNbO₃. The powders after the above mentioned heat treatment did not show any change in Tc on cycling the temperature between 800°C -1200°C [Figure 30]. This confirms that the reaction between LiNbO₃ and MgTiO₃ is complete and longer heat treatments are not necessary. Longer processing time in fact might lead to loss of lithium. X-ray diffraction was also done on the samples in the step scanning mode. This method of collecting data involves forcing the detector to collect data until a preset count or a preset time is reached. Data collection in the step scanning modes ensures that the peaks of minor phases are detected. Figure 31 shows the data from the step scanning mode between two theta values of 24-29°. Only the silicon peak at 28.4° is seen and peaks of no other phase was observed. Five batches of LiNbO₃ doped with 5% MgTiO₃ were processed. This was done to check the reproducibility of the data and all the five batches produced single phase LiNbO₃.

4.2.1 X-ray diffraction and phase stability

The x-ray diffraction patterns of lithium niobate doped with 5 and 10% magnesium titanate are shown in Figures 32-33. These two patterns show the existence of single phase LiNbO₃. X-ray diffraction patterns of LiNbO₃ doped with up to 25% MgTiO₃ show the existence of single phase LiNbO₃. At 30% doping level (Figure 34) small
Figure 30. DTA plot showing the effect of cycling on the $T_c$ of lithium niobate doped with 5% MgTiO$_3$. The two sets represent consecutive heating runs.
Figure 31. XRD pattern of lithium niobate doped with 5% MgTiO$_3$ in the step scan mode.
Figure 32. XRD pattern of lithium niobate doped with 5% MgTiO$_3$. 
Figure 33. XRD pattern of lithium niobate doped with 20% MgTiO$_3$. 
peaks of the second phase begin to appear. The peaks were indexed and correspond to the phase MgTiO$_3$. Very few peaks of MgTiO$_3$ can be seen in Figure 34 since the diffraction peaks of LiNbO$_3$ and MgTiO$_3$ occur at about the same angle. The intensity of MgTiO$_3$ peaks become more pronounced at the 40% doping level and is shown in Figure 35. The JCPDS card for MgTiO$_3$ and all the other phases indexed are reproduced in Appendix B.

The appreciable amount of solid solubility of MgTiO$_3$ in LiNbO$_3$ is not surprising. The ionic radii of Li = 0.68 Å, Nb = 0.69 Å, Mg = 0.66 Å and Ti = 0.68 Å [Handbook of Chemistry and Physics (1989)] are very close to each other and thus this system would be expected to form a solid solution over a wide range. The solid solubility on the MgTiO$_3$ rich region of the system in fact extends up to 43% MgTiO$_3$ [Leibertz and Rosenstein (1969)].

The lattice parameters for the different compositions in this system were calculated using both x-ray diffraction and neutron diffraction. Both measurements agree qualitatively and the results from neutron diffraction were used for this particular system. The lattice parameters from neutron diffraction were used as the conditions for lattice parameter measurement and the program to calculate lattice parameters from x-ray data had not been fully established at this stage of the project.

The variation in the lattice parameters a and c for the MgTiO$_3$ system is shown in Figure 36. The a and c values for LiNbO$_3$ doped with TiO$_2$ [Gallagher and O’Bryan (1988)] are
Figure 34. XRD pattern of lithium niobate doped with 30\% MgTiO$_3$. 

x-Peaks of the second phase (MgTiO$_3$)
Figure 35. XRD pattern of lithium niobate doped with 40% MgTiO$_3$. 

x-Peaks of the second phase (MgTiO$_3$)
Figure 36. The a and the c axis parameter variation in MgTiO₃ and TiO₂ doped systems [1 refers to values taken from Gallagher et al. (1988)].
also added for comparison. It can be seen from Figure 36 that there is a gradual decrease in both the a and the c parameter on the addition of MgTiO$_3$ to LiNbO$_3$. This is in contrast to the more drastic decrease in the a parameter on doping with titanium and a much less pronounced decrease in the c axis. One of the disadvantages of doping LiNbO$_3$ with TiO$_2$ has been the strains associated with this anisotropic contraction along the two crystal axes. The relaxation associated with the strain has been found to cause drift in application. Thus from an application point of view MgTiO$_3$, may be a better dopant than TiO$_2$. Some of the other advantages associated with doping using MgTiO$_3$ will be discussed in the subsequent sections.

Figure 37 compares the c/a ratio of LiNbO$_3$ doped with MgTiO$_3$ and TiO$_2$. The increase in the ratio of c/a is more pronounced for the case of doping with titanium than for doping with MgTiO$_3$. The significance of the ratio of c/a will be discussed after the presentation of results on the study of other dopants.

4.2.2 Curie Temperature

Some typical DTA curves showing the Curie transition for the LiNbO$_3$ samples doped with different amounts of magnesium titanate are shown in Figures 38 to 40. The average $T_c$ for the five samples doped with 5% MgTiO$_3$ was found to be $1179 \pm 1.5^\circ$C. The $T_c$ values for the other samples in the MgTiO$_3$ system are the average of two DTA runs on the same sample.
Figure 37. c/a variation in MgTiO₃ and TiO₂ doped systems (1 refers to values taken from Gallagher et al. (1988)).
Figure 38. DTA plots showing the Curie transition in lithium niobate doped with 3% and 5% MgTiO$_3$. 
Figure 39. DTA plot showing the Curie transition in LiNbO₃ doped with 7% and 10% MgTiO₃.
Figure 40. DTA plot showing the Curie transition in LiNbO$_3$ doped with 20% MgTiO$_3$.
The Curie temperature increases with increasing the MgTiO$_3$ concentration. The transitions at the 15% (Figure 40) and 20% doping levels are hard to detect and beyond 20% it is impossible to determine the $T_c$ using a DTA. The Curie transition is a weak second order transition and the enthalpy associated with Curie transition is masked by the large enthalpy associated with melting. The same problem of the Curie transition being masked by melting has been reported for stoichiometric LiNbO$_3$. Electrical measurements are not attractive for the determination of $T_c$ in LiNbO$_3$ due to the long time the sample has to be maintained at the high temperature. The high temperature leads to loss of lithium and introduces additional errors into the measurement.

The value of $T_c$ for stoichiometric LiNbO$_3$ was determined by studying the thermal expansion in single crystals [Gallagher and O'Bryan (1985)]. Attempts to determine the value of $T_c$ using a dilatometer for polycrystalline samples doped with MgTiO$_3$ was not successful. Lithium niobate expands along the a axis on heating and contracts along the c axis (Figure 10). In a polycrystalline sample the net change is diminished and it is difficult to determine $T_c$.

The variation in $T_c$ as a function of the concentration of MgTiO$_3$ is shown in Figure 41. This result is in conflict with the model that is currently in use to account for variation in $T_c$ with doping [Gallagher and O'Bryan (1988)]. The $T_c$ is related directly to the cation vacancy concentration in that model by the relation
Figure 41. The variation in the $T_c$ of LiNbO$_3$ on doping with MgTiO$_3$. 
\[ T_c (^\circ C) = 1204 - 3280 \text{ CV} \quad (4.6) \]

where CV is the concentration of cation vacancies.

It was thought at the beginning of this study that the doping of LiNbO\(_3\) with MgTiO\(_3\) would not affect the concentration of cation vacancies and hence the \( T_c \). Substantial efforts were taken to ensure that the observed increase in \( T_c \) (Figure 41) was real and not due to some errors involved in the processing step.

The Curie transition in LiNbO\(_3\) doped with 5\% MgTiO\(_3\) was found to be 1179 °C. It was initially thought to be the result of non-stoichiometry of the starting powders of MgTiO\(_3\). Subsequent experiments with MgTiO\(_3\) from a different manufacturer and a mixture of equal moles of MgO and TiO\(_2\) resulted in a similar increase in the Curie temperature. The assay value for this particular batch of MgTiO\(_3\) was obtained from the manufacturer and the following calculation shows that the difference in the starting composition cannot account for the observed change in \( T_c \) with doping.

\[
\begin{align*}
\text{Amount of MgTiO}_3 \text{ added to LiNbO}_3 &= 0.2152 \quad (4.7a) \\
\text{Amount of TiO}_2 &= 0.1390192 \quad (4.7b) \\
\text{Moles of TiO}_2 &= 0.00174 \quad (4.7c) \\
\text{Moles of MgO} &= 0.00189 \quad (4.7d) \\
\text{Excess MgO present (Worst case scenario)} &= 0.00015 \quad (4.7e) \\
\text{Cation Vacancy} &= 0.02067 - 0.3333Z \quad (4.7f) \\
(CV)_{\text{Equimolar Mg & Ti}} &= 0.02067 \quad (4.7g) \\
(CV)_{\text{Titanium Deficient}} &= 0.02062 \quad (4.7h)
\end{align*}
\]
\[ T_c (\degree C) = 1204 - 3280(CV) \] [Gallagher and O'Bryan (1988)](4.7i)

Based on this relation

\[ [T_c (\degree C)]_{\text{Equimolar Mg and Ti}} = 1136.20\degree C \] (4.7j)
\[ [T_c (\degree C)]_{\text{Titanium Deficient}} = 1136.36\degree C \] (4.7k)

Thus the deviation in stoichiometry of magnesium and titanium cannot account for the observed increase in \( T_c \). As an extra precaution, digital channel maps from the sample were compared for the distribution of magnesium, titanium and niobium (Figure 42). This was done to ensure that there was no undissolved titania in the sample. If some titania remains undissolved, there would be excess MgO dissolved in the LiNbO\(_3\) and this could account for the increase in \( T_c \). It is observed from the digital channel map (Figure 42), the distribution of magnesium and titanium is uniform and no second phases could be detected in the sample. The x-ray diffraction pattern in the step scan mode [Figure 31] does not show any peaks of TiO\(_2\). It was also observed that on cycling the sample between 1100 and 1200\degree C the \( T_c \) did not change [Figure 30]. If some undissolved second phase exists, the second phase should dissolve in the matrix at the high temperature. If this happens, the \( T_c \) should change between the first and the second cycle.

Figure 43 shows the typical particle size distribution in the processed powders of 1\% and 5\% MgTiO\(_3\) doped powders. The particles had a size distribution in the range of about
Figure 42. Digital channel map showing the distribution of cations in the sample doped with 5% MgTiO₃ [Top left - Titanium, Top right - Niobium, Bottom left - Magnesium and Bottom right - The micrograph].
Figure 43. SEM micrograph of the powdered samples doped with magnesium titanate [Top - 1% dopant and Bottom - 5% dopant].
3-8 μm. There is no report in the literature of particle size influencing the $T_c$ in LiNbO$_3$ and the DTA curves indicates a single step transition. All of this data together confirms that the observed increase in $T_c$ is real and not the result of some errors introduced in the processing step.

It is seen from Figure 41 that the rate of increase in $T_c$ follows a two-step process. The $T_c$ increases rapidly up to about the 4% doping level and then gradually beyond that point. A similar threshold behavior has been observed in the case of doping with MgO also [Bryan et al. (1985)]. On doping with MgO, the Curie temperature increases to 1205°C at about 4.5% doping level and remains a constant beyond this level of doping [Grabmaier et al. (1991)].

It was suspected that the site occupancy of the dopants might be changing at higher concentration of dopants. As discussed in the literature review (Chapter 2), there is no conclusive evidence for the site occupancy of the dopants. In the very few attempts that have been made to ascertain the site occupancy, Ti$^{4+}$ ions have been assigned lithium sites [Hauer et al. (1994)] and Nb sites [Buchal et al. (1988)]. Magnesium ions have been assigned to lithium sites from a simple electrical charge misfit consideration [Dunbar (1989)]. This is the first study in which neutron diffraction has been used to identify the sites occupied by the dopants. The sites occupied by magnesium and titanium as a function of dopant concentration is shown in Figure 44. Magnesium occupies lithium sites while titanium occupies the niobium sites across the entire region of solid solubility. This study is unambiguous in that the magnesium occupies lithium sites and titanium occupies
Figure 44. Site occupancy of magnesium and titanium in LiNbO$_3$ doped with MgTiO$_3$. 
niobium sites. Any refinement that forced titanium on the lithium site or magnesium on the niobium site did not give results consistent with the observed neutron diffraction pattern.

The increase in $T_c$ on doping with MgTiO$_3$ cannot be explained on the basis of the cation vacancies alone determining the $T_c$ of LiNbO$_3$. There is no report in the literature of this two step increase in $T_c$ with doping. It is interesting to note that the $T_c$ shows a change in behavior at exactly the same concentration of dopants as the vacancy concentration in the undoped LiNbO$_3$. Thus it seems that the $T_c$ shows a threshold in behavior when the $[\text{Li}^+\text{Mg}]$ concentration is equal to the lithium concentration in the stoichiometric composition. The significance of this two step variation in $T_c$ and other theories associated with the role of dopants in $T_c$ will be discussed after the presentation of data on the effect of other dopants on the properties of LiNbO$_3$.

4.2.3 Refractive Index

In order for LiNbO$_3$ to be used as a waveguide, the dopant should cause an increase in the refractive index (RI) of LiNbO$_3$. The refractive index of LiNbO$_3$ doped with 5% MgTiO$_3$ was measured. The extraordinary RI of the starting LiNbO$_3$ was found to be 2.222 ± 0.005 and the ordinary RI was found to be greater than 2.25. These values are close to the values reported in the literature. [Bergman (1968)] The ordinary RI for the powders doped with 5% MgTiO$_3$ was found to be greater than 2.25, while the extraordinary RI was found to be greater than 2.222 but less than 2.233.
Measurement of the refractive index could not be done on more samples due to the high cost. The results of the RI studies are preliminary and was done just to investigate the feasibility of MgTiO₃ as a dopant for waveguide applications. But the extraordinary refractive index does increase on doping with MgTiO₃. In the case of doping with titania, the observed increase in refractive index has been attributed to the lattice contraction from titanium substitution [Sugii et al. (1978), Atuchin et al. (1989)]. The lattice also contracts on doping with MgTiO₃ and thus an observed increase in RI on doping with MgTiO₃ agrees with these theories.

4.2.4 Advantages of MgTiO₃ as a dopant for LiNbO₃

The main disadvantage of titania doped waveguides has been the decrease in Tc with the concentration of TiO₂. In order to maintain the single domain structure of LiNbO₃, the diffusion temperature for the formation of waveguides has to be kept below 950°C. This low temperature of diffusion anneal prevents the formation of well defined waveguides. On the other hand, doping LiNbO₃ with MgTiO₃ increases the Curie temperature and thus the temperature of diffusion can be increased without damaging the quality of the single crystal. An increase in the temperature of diffusion would increase the production efficiency in addition to enabling the formation of well defined waveguides.

The a and c parameters contract more uniformly on doping with MgTiO₃. The waveguides formed by doping with TiO₂ set up non-uniform strains and the subsequent relaxation results in the problem of drift [Gallagher & O’Bryan (1988)]. The uniform
contraction on doping with MgTiO₃ may lead to less problems with drift in devices characteristics.

Lithium niobate doped with titania suffers from photorefractive damage [Bryan et al. (1985)]. Addition of a few percent of magnesia reduces the photorefractive damage drastically [Volk et al. (1990)]. Lithium niobate doped with 4.6% MgO has been experimentally found to withstand about one hundred times higher optical intensity than the undoped LiNbO₃. This decrease in the photorefractive damage is attributed to the higher photoconductivity in the presence of magnesium. Bryan et al. (1985) mention clearly that they have not determined the cause for the decrease in the photorefractive damage, they suggest alteration in the energy levels of impurity as a possible reason for the observed difference. It has been suggested by Arizmendi et al. (1987), that doping with MgO decreases the concentration of traps that restrict charge mobility. This increase in mobility of the charge carriers has been suggested as the reason for the decrease in photorefractive damage. The decrease in photorefractive damage of LiNbO₃ with MgO has been observed but no real explanation exists for this phenomenon. But it is possible, that the magnesium in MgTiO₃ would also decrease the photorefractive effect, and this would enable the waveguides to withstand higher optical intensity.

4.3 STUDY OF OTHER DOPANTS IN LiNbO₃

As a completely consistent picture for the dependence of the Curie temperature on dopant did not evolve from the study on MgTiO₃ system, other dopants were studied.
Information on the solid solubility of the dopants in LiNbO₃, the phases that are evolved at the limit of solid solubility and the effect of the dopants on the Curie temperature and lattice parameter are not available. Investigation of the phase diagrams and other properties would enable LiNbO₃ doped with other oxides to be used for applications like optical frequency doubling, parametric oscillation and other phase-matching processes.

Some of the key x-ray diffraction patterns for LiNbO₃ doped with the different oxides are shown in Figures 45-52. The limits of solid solubility and the second phases that appear beyond the limit of solid solubility are summarized in Table 11. There are no published phase diagram for most of the systems given below. This is the first attempt to determine the second phases evolved at the limit of solid solubility in the ZnO, CaO and ZrO₂ system. The variation in the lattice parameters, volume and the c/a ratio are shown in Figures 53-58.

Table 11. Summary of the x-ray diffraction study

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Limit of solid Solubility (%)</th>
<th>Second Phase</th>
</tr>
</thead>
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<tr>
<td>MgTiO₃</td>
<td>25-30</td>
<td>MgTiO₃</td>
</tr>
<tr>
<td>ZnO</td>
<td>10-15%</td>
<td>LiZnNbO₄</td>
</tr>
<tr>
<td>MgO</td>
<td>10-15%</td>
<td>Li₃NbO₄, Nb₂O₅</td>
</tr>
<tr>
<td>CaO</td>
<td>5-10%</td>
<td>Li₃NbO₄, Ca₂Nb₂O₇</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>&lt; 5</td>
<td>LiVO₃</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>&lt; 5</td>
<td>ZrO₂</td>
</tr>
</tbody>
</table>
Figure 45. XRD pattern of lithium niobate doped with 5% MgO.
Figure 46. XRD pattern of lithium niobate doped with 15% MgO.
Figure 47. XRD pattern of lithium niobate doped with 15% ZnO.

- Peaks of the second phase LiZnNbO$_4$
Figure 48. XRD pattern of lithium niobate doped with 25% ZnO.
Figure 49. XRD pattern of lithium niobate doped with 10% CaO.
Figure 50. XRD pattern of lithium niobate doped with 5% NiO.
Figure 51. XRD pattern of lithium niobate doped with 10% ZrO$_2$. Peaks of the second phase ZrO$_2$. 
Figure 52. XRD pattern of lithium niobate doped with 5\% V\textsubscript{2}O\textsubscript{5}.

- Peaks of the phase LiVO\textsubscript{3}.
Figure 53. Variation in the lattice parameter 'a' on doping with divalent oxides.
Figure 54. Variation in the lattice parameter 'c' on doping with divalent oxides.
Figure 55. Variation in the volume of the unit cell on doping with divalent oxides.
Figure 56. Variation in the c/a axis ratio on doping with divalent oxides.
Figure 57. Variation in the c/a axis ratio on doping with tetravalent oxides (1 refers to values taken from Gallagher et al. (1988)).
Figure 58. The a and the c axis parameter variation in ZrO$_2$ and TiO$_2$ doped systems [1 refers to values taken from Gallagher (1988)].
The data from the DTA, that show Curie transition in the LiNbO₃ doped with the different oxides are shown in Figures 59-64. The variations in the $T_c$ as a function of the dopant concentration are shown in Figures 65 and 66.

4.3.1 Magnesium Oxide System

Among all the system reported in Table 11, only the LiNbO₃-MgO system has been investigated in some detail [Grabmaier et al. (1985)]. The solid solubility limit of MgO in LiNbO₃ was found to be between 25-30% [Hu et al. (1991A)]. In this study peaks of the second phase appear at the 15% doping level. The reason for the differences between this study and the earlier studies could be attributed to the earlier studies [Grabmaier(1986) and Hu(1991B)] used single crystals while this work was done on powders. In single crystals samples the lithium content of the crystal and the distribution coefficient of magnesium between the melt and the crystal varies as a function of the magnesium concentration (Figure 16). In this study, the lithium concentration is maintained constant at the different doping levels. It is seen from figure 16 in the case of single crystals, that the lithium concentration decreases by about 4% on going from undoped LiNbO₃ to 6% MgO level. This loss of lithium would favor dissolution of more magnesium in single crystal samples.

It is seen from Figures 68 and 69 that both the $a$ and $c$ parameters decrease initially and then begin to increase. The $a$ and $c$ parameters reach a minimum value at the doping level of about 5% before they begin to increase. This differs from the earlier studies in
Figure 59. DTA plot showing the Curie transition in lithium niobate doped with 5% MgO.
Figure 60. DTA plot showing the Curie transition in LiNbO$_3$ doped with 5% ZnO.
Figure 61. DTA plot showing the Curie transition in LiNbO$_3$ doped with 10% ZnO.
Figure 62. DTA plot showing the Curie transition in LiNbO$_3$ doped with 5% CaO.
Figure 63. DTA plot showing the Curie transition in lithium niobate doped with 5% and 10% ZrO$_2$. 
Figure 64. DTA of lithium niobate doped with 5% vanadium oxide ($V_2O_3$).
Figure 65. Variation in the Curie temperature of LiNbO$_3$ with the concentration of divalent dopants.
Figure 65. Variation in the Curie temperature of LiNbO$_3$ with the concentration of divalent dopants.
Figure 66. Variation in the Curie temperature of LiNbO$_3$ with the concentration of tetravalent dopants.
which the lattice parameters were found to increase with magnesium concentration. This observed difference again be attributed to the continuous change in the lithium concentration with magnesium doping in single crystal samples. The lithium concentration in the study by Grabmaier(1991) drops from 48.2% to 45% when the MgO level reaches 6%. The change in the lattice parameter in the case of single crystal will be affected by this change in the lithium concentration. In the study by Hu et al. (1991B), the lattice parameter continuously increases until the limit of solid solubility. But at about the 7.5% doping level the distribution coefficient of magnesium between the melt and the crystal changes abruptly from 1.2 to 0.97. The continuous change in the concentration of lithium and magnesium in the earlier studies makes it difficult to compare the studies. It is interesting to note that the distribution coefficient changes in the earlier studies at approximately the same composition at which the lattice parameter shows a different behavior in this study.

It is unique that the lattice parameter initially decreases and then begins to increase within the same solid solution region. This behavior indicates that the mechanism for incorporation of the dopant changes at about the 5% doping level. As LiNbO$_3$ doped with ZnO exhibit properties similar to that of MgO, possible explanations for this phenomenon will be presented after the presentation of data on the ZnO system.

The Curie transitions on doping with MgO occur close to the melting point and are difficult to detect (Figure 59). It is seen from Figure 65, that the $T_c$ increases initially and then begins to drop. The variation in the $T_c$ is a mirror image of the observed behavior in lattice parameter and shows a maximum at the 5% doping level. The variation in $T_c$ is
qualitatively similar to the earlier work on LiNbO$_3$-MgO system. In the work by Grabmaier et al. (1991), variation in $T_c$ was studied only up to 8% and so the decrease in $T_c$ was not observed. In the study by Hu et al. (1991B), after an initial increase a decrease in $T_c$ was observed. But at a MgO doping level between 5 and 12% there was not any appreciable change in $T_c$. The difference between the work reported here and the work of Hu et al. (1991B) can be attributed to the change in magnesium distribution at about this point. The reasons for the increase in $T_c$ will be discussed after the presentation of data on other systems.

4.3.2 Zinc Oxide System

There is only one reported study in the literature on the LiNbO$_3$-ZnO system [Kawakami et al. (1986)]. The work by Kawakami was done by substituting Zn for Li, thereby making solid solution of the type (Li$_{1-x}$Zn$_{x/2}$)NbO$_3$. His starting composition is not clearly mentioned and the second phase that appears at the limit of solid solubility has not been identified.

The limit of solubility of ZnO in lithium niobate as determined by this study by addition is between 10 and 15%. The limit of solid solubility by substitution as reported by Kawakami is about 25%. Figure 55 clearly identifies LiZnNbO$_4$ as the second phase that is precipitated at the limit of solid solubility. This is the first time, precipitation of LiZnNbO$_4$ beyond the limit of solubility of ZnO in LiNbO$_3$ has been reported. The $a$ and $c$ lattice parameters show a behavior that is identical to the case of MgO doping.
The work by Kawakami (1985) shows a continuous increase in the a and c parameters. The difference in the lattice parameter and the limit of solubility between this study and the study of Kawakami is attributed to earlier mentioned differences between single crystal samples and powder samples.

The DTA plots showing the Curie transition for ZnO doped samples are shown in Figures 60 and 61. The initial increase and the subsequent decrease in $T_c$ is seen in Figure 65. The Curie transitions are easier to identify in the case of doping with ZnO, as the $T_c$ is far below the melting temperature of the composition. Qualitatively all the properties of the zinc oxide doped system ($a$, $c$, $T_c$ and $c/a$) are similar to the MgO system. Kawakami (1986) reports a decrease in $T_c$ on doping with zinc. His polycrystalline sample (Figure 19) without the addition of any dopant shows a $T_c$ of 1190°C and data only beyond the 10% doping level was presented. So it is hard to comment on his data, without the knowledge of the starting composition or the behavior at the 5% doping level.

Results of the neutron diffraction study on ZnO samples are shown in Table 12. These results were arrived at by refining the site occupancy of the dopants. The data for site occupancy that gave the best fit between the observed pattern and the refined parameters are given below.
Table 12. Site occupancy data for ZnO doped samples

<table>
<thead>
<tr>
<th></th>
<th>5% ZnO</th>
<th>10% ZnO</th>
<th>15% ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li Site %</td>
<td>Li 95(0.3)#</td>
<td>Li 91.3%</td>
<td>Li 88.0%</td>
</tr>
<tr>
<td></td>
<td>Zn 5%</td>
<td>Zn 8.7%</td>
<td>Zn 12.0%</td>
</tr>
<tr>
<td>Nb Site %</td>
<td>Nb 100%</td>
<td>Nb 98.7%</td>
<td>Nb 97.0%</td>
</tr>
<tr>
<td></td>
<td>Zn 1.3%</td>
<td>Zn 1.3%</td>
<td>Zn 1.3%</td>
</tr>
<tr>
<td>O Site %</td>
<td>99.5% (4)*</td>
<td>98.8 % (6)*</td>
<td>99.2 % (6)*</td>
</tr>
</tbody>
</table>

#The errors in the site occupancy of cations is about 0.3%
*The values in parentheses give the variation in the last significant digit.

The above results were obtained by constraining the zinc concentration to be equal to the initial dopant concentration and the cation occupancy to be 100%. At a doping level of 5% all the zinc ions occupy lithium sites, while at the 10% and 15% level zinc ions are found on both the sites. Due to the large number of variables involved some constraints have to be enforced to arrive at meaningful values. The neutron diffraction results are a function of the constraints enforced and thus the results should be interpreted with certain amount of caution.

Although this data is open to different interpretation, the data proves conclusively that the zinc occupies both the lithium and niobium sites beyond a threshold level of dopant concentration. Any constraint that forced all the zinc to go to the lithium site on doping with 10% ZnO resulted in the lithium site occupancy being over 100%. Thus it was concluded that zinc occupies both lithium and niobium sites.
Oxygen vacancies were considered as possible defects in LiNbO$_3$ on doping with ZnO. The reaction

$$2\text{ZnO} \rightarrow \text{LiNbO}_3 + \text{Zn}^{1+}_\text{Li} + \text{Zn}^{1+}_\text{Nb} + \text{V}^{2+}_O + 2\text{O}^\circ \quad (4.8)$$

ensure both charge and site balance. There has been no report of oxygen vacancies in the LiNbO$_3$ system. In fact Smyth (1983) has not found any evidence for oxygen vacancies using electrical conductivity measurement in MgO doped samples. According to Smyth, the intrinsic ionic disorder is dominant due to the energetic equivalence between the LiNbO$_3$ and ilmenite stacking sequence and the effect on conductivity due to the dopants is small. The neutron diffraction data agree that there is no additional dominant defect, even at high concentration of dopants. If equation 4.12 were to hold good, oxygen vacancies should actually increase on going from 10% to the 15% doping level. The occupancy at the oxygen site actually increases on going from the 10% to 15% doping level. Thus based on the refinement results obtained so far, oxygen vacancies does not appear to be a dominant defect in LiNbO$_3$.

In addition, computer modeling studies [Donnenberg (1991)] have suggested self-compensation as the most likely mechanism for charge compensation in LiNbO$_3$. According to the self-compensation theory, the dopant would occupy Li and Nb sites and the ratio of occupancy would be determined by the charge of the dopant. As an example divalent dopants would occupy Li and Nb sites in the ratio of 3:1 while trivalent dopants would occupy both sites equally. According to them, doping The occupancy at the
oxygen site actually increases on going from the 10% to 15% doping LiNbO₃ with ZnO should be expressed as

\[
4ZnO \xrightarrow{LiNbO_3} 3Zn^{1+} + Zn^{2+} + 4O^{2-}
\]  

(4.9)

The above solution does not maintain the cation to anion ratio in LiNbO₃. The energy for the creation of oxygen vacancies was found to be always higher than that for self compensation [Table 6]. In the case of doping with divalent oxides, creation of \((Li_{v})^{4+}\) was proved to be more energetically favored than the creation of oxygen vacancies. But even this defect has not been experimentally observed so far.

In short there is no conclusive proof for the mechanism of substitution and charge compensation for any of the dopants so far. Further variations in the refinement procedure are currently being tried to understand the phenomenon further.

4.3.3 Nickel Oxide System

Only two compositions (5 and 10%) were studied in the nickel oxide system. The ionic radii of nickel (0.68 Å) makes it a suitable dopant for the LiNbO₃ system. The solid solubility limit was not reached at the 10% doping level and the lattice parameters show a well pronounced decrease with the addition of NiO. The Curie temperature for both the compositions could not be identified probably due to the \(T_c\) being near the melting point. Further work was not done on this system due to the inability to identify \(T_c\).
4.3.4 Calcium Oxide System

There is no report in the literature of any work on LiNbO$_3$-CaO system. The large size of the Ca$^{2+}$ (0.99 Å) would probably account for this system not having been investigated. The limit of solid solubility for CaO in LiNbO$_3$ is about 5-10% and peaks of the second phase Li$_3$NbO$_4$ and Ca$_2$Nb$_2$O$_7$ are visible in the x-ray diffraction pattern. The large ionic size is responsible for the low solubility of CaO in LiNbO$_3$. The lattice parameter increases and the c/a ratio decreases on doping. The Curie temperature decreases with CaO doping and this behavior is different from any of the other divalent systems investigated.

4.3.5 Miscellaneous Systems

In order to better understand the role of dopants on the properties of LiNbO$_3$, tetravalent (Zr, Ti) and pentavalent (V) dopants were also added to LiNbO$_3$. Lithium niobate powders doped with titania has been investigated before [Gallagher and O’Bryan (1988)]. The titania system was investigated in order to see if this study qualitatively agrees with the previous results. This would provide a measure of the reliability of this study. There has not been any previous work on the zirconium or the vanadium systems. The titania is a single phase at a doping level of 15% and agrees with previous work in the literature. The lattice parameters a and c decrease on doping while the c/a ratio increases. The Curie temperature decreases with titania doping and thus the trends of all the parameters investigated (a, c, c/a and $T_c$) agree with the literature.
The limit of solubility of zirconium in LiNbO$_3$ appears to be near 5%. At the doping level of 10%, peaks of the second phase ZrO$_2$ can be very clearly seen (Figure 51). The lattice parameter $a$ increases by a very small amount, while $c$ decreases (Figure 58). The lattice parameters $a$ and $c$ do not change substantially between 5% and 10%, indicating the limit of solubility is very close to 5%. The low level of solubility of Zr$^{4+}$ with an ionic radii of 0.79 Å is surprising. Calcium (0.99 Å) has about the same or higher level of solubility than zirconium. This is probably due to the calcium and zirconium occupying different sites in the host lattice. A charge misfit criterion would indicate that Ca$^{2+}$ would occupy lithium sites and zirconium would occupy niobium sites. Even though there are disagreements about the defect chemistry at room temperature, Dunbar(1993) has proposed vacancies of lithium as the dominant defect at high temperature. As there are inherently more vacancies at the lithium site, it is possible that solubility of calcium is higher. Doping with zirconia also decreases the $T_c$ and the Curie temperature is unchanged between the 5% and 10% doping level. This again confirms the limit of solubility to be close to 5%.

The vanadium doped powders showed some melting even at the processing temperature of 1100°C. The x-ray diffraction pattern, even at a doping level of 5%, showed the existence of the second phase LiVO$_3$ and the peaks of LiVO$_3$ are more pronounced at the doping level of 10% (Figure 52). The DTA of LiNbO$_3$ doped with 5% V$_2$O$_5$ (Figure 64) indicates melting at about 650°C and this temperature corresponds to the melting point of LiVO$_3$. As a single phase composition could not be developed for the LiNbO$_3$-V$_2$O$_5$ system, this system was not investigated further.
4.4 COMPARISON OF THE PREVIOUS MODELS FOR THE $T_c$ DEPENDENCE ON THE COMPOSITION AND INSIGHTS FROM THIS STUDY.

There have been a number of theories over the years to explain the dependence of $T_c$ on the composition of LiNbO$_3$. All these theories were reviewed in earlier sections and Table 12 summarizes the results of the different studies.

Table 13. Models to account for $T_c$ Variation

<table>
<thead>
<tr>
<th>$T_c$ Dependence</th>
<th>Proof</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>c/a</td>
<td>$T_c$ in Zinc decreases with c/a</td>
<td>Kawakami et al. (1985)</td>
</tr>
<tr>
<td>Cation Vacancies</td>
<td>Li deficiency and Ti addition have same effect</td>
<td>Gallagher and O'Bryan (1988)</td>
</tr>
<tr>
<td>Nb site occupancy</td>
<td>Mg doping increases $T_c$</td>
<td>Grabmaier et al. (1991)</td>
</tr>
<tr>
<td>Li/Nb ratio</td>
<td>$T_c$ increases on going from congruent to Stoichiometric composition</td>
<td>Guenais et al. (1981) and numerous other studies.</td>
</tr>
</tbody>
</table>

All the parameters listed above are not independent and in fact are closely related to each other. For example, changing the Li/Nb ratio would affect the niobium site occupancy, the cation vacancy concentration and the lattice parameters. Thus the relationship developed are based upon the specific parameters that the authors have selected. But the larger question is about the universal validity of any of these criteria for the dependence
of $T_c$ on the composition of LiNbO$_3$. It is seen from Table 13, that the criterion for the
dependence of $T_c$ has been developed after study of only one or two specific systems.
Comparisons between the different studies are difficult due to the variation in the
composition of the crystal or powder from one study to the other. The same difficulty has
been encountered in the analysis of data on diffusion in LiNbO$_3$ [Dunbar (1993A)]. The
data on diffusion actually vary over eight orders of magnitude. The applicability of the
above models to the results of this study will be briefly reviewed.

4.4.1 c/a ratio

It has been proposed that the change in the c/a ratio determines $T_c$ [Kawakami et al.
(1985)]. The decrease in the ratio of c/a on substituting zinc for lithium had been used to
explain the drop in $T_c$. Even without taking into account the present study, it has been
reported that the c/a ratio on doping with titania increases while the $T_c$ decreases. It is
seen from Figure 37, that the c/a ratio for both MgTiO$_3$ and TiO$_2$ increases while $T_c$
shows opposite behavior.

The results from the studies on other dopants (Figures 56 and 57) do not support this
theory either. But an extensive study by Torii et al. (1983) on LiTaO$_3$ doped with
divalent oxides support this theory. Although LiNbO$_3$ and LiTaO$_3$ are similar in a lot of
respects their dielectric properties and Curie temperatures are very different [Lines
(1969)]. The $T_c$ of LiTaO$_3$ is about 600°C, nearly 500°C less than that of LiNbO$_3$. This
difference in $T_c$ has been attributed to the greater covalency and greater strength of the
tantalum-oxygen bond. The greater degree of covalency decreases the effective point charge and thus decreases the dipolar forces in LiTaO$_3$ with respect to LiNbO$_3$. This decrease in dipolar force results in a decrease in $T_c$. Thus a theory developed to explain the dependence of $T_c$ in LiTaO$_3$ need not necessarily apply to the LiNbO$_3$ system due to the difference in the nature of bonding in the two systems.

The study on LiTaO$_3$ correlating $c/a$ with $T_c$ has been developed after study only on divalent systems and has not widely tested. On the contrary in this study, the MgO system has the maximum decrease in $c/a$ (Figure 56) while the increase in $T_c$ is a maximum. In fact $c/a$ and $T_c$ show opposing trends in the divalent systems. If $c/a$ is the critical factor, $c/a$ should also change direction when the magnitude of $T_c$ changes at the 5% doping level in the MgO and ZnO systems. Thus it is concluded from this study that the $c/a$ is not the critical factor in determining $T_c$ of LiNbO$_3$.

4.4.2 Cation Vacancy

The present work was started on the assumption that the cation vacancies control $T_c$. There is excellent agreement between the cation vacancy concentration (CV) and the $T_c$ in the simple lithium deficient and with the TiO$_2$ system. But this $T_c$ dependence on CV has not been universally observed in this study. If the CV model holds true, there should be no change in $T_c$ on doping with MgTiO$_3$ and the effect of adding MgO and ZnO to LiNbO$_3$ should be the same. It is seen from Figures 41 and 65 that this behavior is not observed. Theories for the Curie transition of LiNbO$_3$ have been influenced by work on
perovskite-type oxide [Johnson et al. (1979)]. The perovskites show a well characterized
dependence of $T_c$ on the CV. But there are significant differences between the perovskite
systems and LiNbO$_3$.

The A and B cations in the perovskites have a well defined size difference and occupy
distinct sites in the lattice. The smaller cation has six near neighbors while the larger
cation has 12 near neighbors. The size of the dopant ion determines the number of near
neighbors it can support and hence the site occupied by the dopant. The distinct
environment around the two cations also eliminates the problem of site swapping.

In addition, the $T_c$ of the perovskite oxides are much lower and electrical characterization
techniques and high temperature x-ray diffraction can be used to understand the
mechanism of the Curie transition. But even in perovskites, the mechanism of Curie
transition has not been fully established [Igarshi et al. (1987)]. Thus enough knowledge
is not available about the LiNbO$_3$ to correlate to a single parameter. It is not essential
that even if further information is available about the LiNbO$_3$ system, that a single
parameter has to explain the dependence of the $T_c$ on the dopant concentration.

Although the titanium system is widely used, there is no discussion in the literature on the
defects created on doping with TiO$_2$. The reason for this lack of discussion will be
pointed out later. It is concluded from this study that the CV concentration alone does
not determine the $T_c$. 
4.4.3 Niobium Site Occupancy

The niobium site occupancy model is a slight variation of the cation vacancy model. According to the model of Abrahams and Marsh, vacancies occur only at the niobium site. As one moves from the congruent to stoichiometric composition, the number of vacancies at the niobium site is reduced and an increase in the Curie temperature is observed. Thus the niobium occupancy model states that only the occupancy of the niobium sites control the $T_c$. It is hard to imagine that the lithium disordering which leads to the ferroelectric to the paraelectric transition is not influenced by the occupancy or the ion at the lithium position. This model has very little data to support it.

4.4.4 Li/Nb ratio

The Li/Nb ratio fails to explain the observed behavior of $T_c$ in the MgTiO$_3$, MgO and ZnO systems. The Li/Nb ratio should be altered by the same amount on doping with equal moles of MgO and ZnO. The change in $T_c$ is not the same on doping with equal moles of MgO and ZnO. Thus the Li/Nb ratio also fails to explain adequately the observed dependence of $T_c$ on the composition of the LiNbO$_3$.

It is clear from the above discussion, that none of the above mentioned parameters or models have been able to explain the dependence of $T_c$ for all of the oxides.
4.4.5 Trends observed in $T_c$ by this study.

Some of the trends observed $T_c$ will be briefly highlighted. This is the first study on doping LiNbO$_3$ with di-, tri- and tetra-valent dopants. The tetravalent dopants (Zr & Ti) show a decrease in $T_c$ on doping. The magnitude of this decrease is not the same for the two dopants.

The divalent (Mg and Zn) and the trivalent (MgTiO$_3$) dopants show a two-step behavior. In the case of the divalent dopants, $T_c$ increases initially and this is accompanied by a decrease in both the a and the c lattice parameters. Beyond the 5% doping level the $T_c$ decreases and the a and the c parameters increase. The relation between the lattice parameter and $T_c$ in the case of divalent systems seems to be significant. The CaO system shows a decrease in $T_c$ and the a parameter increases. But the lattice parameter measurement in the case of doping with 5% CaO had large errors (ESD a = 0.001Å and ESD c=0.002 Å) and so this trend was not taken into consideration.

On doping with MgTiO$_3$ the rate of increase in $T_c$ follows a two-step behavior. The rate of increase is steep up to about 4% doping level and increases more gradually beyond this point. It seems from studies on MgTiO$_3$, ZnO and MgO, doping levels up to the point at which the inherent vacancies of LiNbO$_3$ are filled, the $T_c$ increases. Doping levels of about 4 to 5% on the lithium site would correspond to the stoichiometric composition. At about this point there is a change in behavior. The incorporation mechanism of the dopant changes beyond this point and the $T_c$ begins to show a different behavior. The
Mg$^{2+}$ and Ti$^{4+}$ ions in the case of doping with MgTiO$_3$ continue to occupy Li and Nb sites. There is a slow increase in $T_c$ beyond the 5% doping level.

In the case of doping with zinc it has been shown by neutron diffraction that zinc ions occupy both the lithium and the niobium sites beyond the 5% doping level. The niobium octahedron is smaller than the lithium octahedron. Incorporation of the zinc ion in the niobium site would lead to an increase in the lattice parameters. This result is consistent with the initial decrease in the lattice parameter and an increase in the lattice parameter at the point at which zinc is found to occupy both lithium and niobium sites.

It is hard to speculate what happens beyond this point. Even in a widely studied system like the TiO$_2$-LiNbO$_3$, there is no discussion on the site occupancy of the dopants. There has not even been a single speculation in the literature on the defects produced to compensate for titanium doping into LiNbO$_3$. The reason for the lack of discussion though never mentioned in the literature is not surprising. Five possible charged species can occur in this system. The five charged species that can occur are Mg$_{Li}$, Nb$_{Li}$, V$_{Li}$, V$_{Nb}$ and Mg$_{Nb}$. Vacancies of oxygen are not taken into consideration in this analysis as there exists no proof for their existence. A similar set of charged species can be written for any dopant.
For charge balance

\[ 5[V_{Nb}^{5-}] + 3[Mg_{Nb}^{3-}] + [V_{Li}^-] = 4[Nb_{Li}^{4+}] + [Mg_{Li}^+] \]  

(4.10)

and for site balance

\[ [V_{Nb}^{5-}] + [Mg_{Nb}^{3-}] = [Nb_{Li}^{4+}] + [Mg_{Li}^+] + [V_{Li}^-] \]  

(4.11)

relations should hold.

As no conclusive evidence exists for the site occupancy of Ti$^{4+}$ ions in the host lattice or for that matter for any other dopants, it is an equation in five unknowns with only two constraints. An additional constraint is available from a knowledge of the titanium concentration. But it is still not enough to explain the defect chemistry and the relationship between the defect chemistry and the Curie temperature.

Neutron diffraction analysis also suffers due to the presence of different types of defects. Some constraints have to be enforced in order to arrive at meaningful values. The concentration levels of some of the defects are below the detectability limit of neutron diffraction. Although the neutron diffraction is able to identify the site occupied by the dopants, a completely consistent picture does not emerge from neutron diffraction.

In conclusion it is hard to attribute control of the $T_c$ of LiNbO$_3$ to a single parameter, with the present level of knowledge in LiNbO$_3$. To begin with, the room temperature defect structure of congruent LiNbO$_3$ is not clearly understood and when dopants are added the site occupancy of the dopants and the charge compensating defects that are produced are not fully established. In addition, at high temperatures, complications arise
from a change in the defect structure [Dunbar (1993A)] and site swapping between the cations [Dunbar and Catchen (1993B)].

It is also essential to remember that the Curie transition in LiNbO$_3$ corresponds to the point at which Li-ions occupy equivalent sites on either side of the oxygen plane and the niobium ions shift to the centrosymmetric position [Tomov et al. (1989)]. In essence the Curie transition corresponds to the ease of disordering of the ions at the lithium sites and movement of the ions at the niobium site to the centrosymmetric position. The above mentioned process will depend on a number of factors like the vacancies and ions at the lithium and niobium sites, the size of the ions, the strength of the bonds and a number of other factors. Thus although the $T_c$ may depend on $c/a$ ratio, $CV$ etc., it is impossible to express $T_c$ as a function of just one of these parameters.
CHAPTER V

CONCLUSIONS

The major conclusions of this study are:

(1) Magnesium titanate has been found to be a suitable dopant for waveguide applications in LiNbO₃. One of the problems associated with the titania doped system was the significant reduction in the Curie temperature of LiNbO₃ with the addition of titania. This decrease in $T_c$ has limited the temperature of diffusion of titanium into LiNbO₃ and prevented the formation of well defined channel waveguides. Magnesium titanate does not suffer from this drawback. The Curie temperature in fact increases on doping with MgTiO₃. This increase in Curie temperature would enable quality waveguides to be produced in substantially less amount of time. In addition, the change in the lattice parameters is more uniform along the two axes on doping with MgTiO₃. This uniform strain would minimize some of the problems associated with the drift in device performance.
(2) The applicability of the currently accepted models to explain the dependence of $T_c$ on composition was tested by doping LiNbO$_3$ with different materials. None of the models currently in use has been found to be universally true. The $T_c$ can not be expressed as a function of just one variable.

(3) Neutron diffraction was able to determine the site occupancy of dopants in LiNbO$_3$. Lithium vacancies were found to be the charge compensating defects in congruent LiNbO$_3$ and this result is not in agreement with the model currently used to account for lithium deficiency. In the case of doping with MgTiO$_3$, the magnesium was found to occupy lithium sites and titanium the niobium sites. Zinc was found to occupy lithium sites up to a threshold level of dopant concentration and then found to occupy both lithium and niobium sites. This change in occupancy of the zinc ion coincides with a change in behavior of the lattice parameter and the Curie temperature. Although neutron diffraction was able to determine the site occupancy of dopants it suffers from two main drawbacks. Due to the many different kind of defects possible in this system, some constraints have to be forced on the refinement process. These constraints will influence the results. Also the concentration and change in concentration of some of the defects on doping are within the detectability limits of neutron diffraction. The above two constraints prevents the development of a complete picture on the effect of doping.
A number of possible research and technological projects can arise from this study.

(1) \( \text{LiNbO}_3 - \text{MgTiO}_3 \) system: This system has to be investigated further before \( \text{MgTiO}_3 \) can be used as a dopant for the formation of waveguides. The diffusion and dissolution of Mg and Ti in \( \text{LiNbO}_3 \) should be understood. More efforts are required in terms of characterizing the optical properties of this system.

(2) \( \text{LiNbO}_3 - \) Divalent systems: Lithium niobate and MgO and ZnO system should be characterized further. More compositions in this system should be investigated to check the dependence on \( T_c \) and lattice parameters.

(3) Site occupancy of dopants: Information on the site occupancy of the cations would provide for better understanding of the defect structure and the role of dopants on the properties of \( \text{LiNbO}_3 \). It has been established that neutron diffraction could be a powerful
technique in determining the site occupancy of dopants. More work on determining the site occupancy of the dopants and the intrinsic defect structure of LiNbO$_3$ using neutron diffraction is recommended.
APPENDIX A

Development of Optical DTA

Paper accepted for publication in Thermochim. Acta
A DTA BASED ON OPTICAL MEASUREMENT
OF TEMPERATURE

Jai Subramanian and P.K. Gallagher

Departments of Materials Science & Engineering and Chemistry
The Ohio State University
Columbus, OH 43210-1173, U.S.A.

A DTA instrument has been designed around the Acufiber Model 100C temperature measurement and control system. The temperature of the sample and reference materials are determined by their black body radiation. This radiation is conveyed through single crystal sapphire light pipes that also act as supports for the sample and reference. The T signal is determined by subtraction and the temperature of the reference material is used to control the furnace temperature. The furnace is manufactured by Harrop and capable of 1700 C.

The sensitivity of the optical sensors, however, is insufficient below about 500 C for proper operation of the system as a DTA. Above this temperature, a variety of transitions and materials have been used to help establish the feasibility of this approach to DTA. Melting points of metals, solid\textsubscript{1} to solid\textsubscript{2} transitions, and second order transitions have been studied. Bulk materials in alumina crucibles were measured and studies on thin films are in progress. Direct viewing of the sample and reference or the use of a exterior coating of Pt black on the crucibles is possible, however, the latter is preferable.

These preliminary investigations have been encouraging and considerations of the effects of emissivity are being explored.

INTRODUCTION - Differential thermal analysis, DTA, has found considerable use for the detection of phase transitions and solid state reactions at elevated temperatures. At temperatures above about 1600 C, however, the conventional use of thermocouples
as temperature sensors becomes very limited and controlled atmospheres are generally required. Their sensitivity drops off and, because of the need for good thermal contact with the sample, the possibilities of reactions with the sample or its holder increase. That same contact with the sample also represents a path of thermal leakage, and hence a perturbation on the measurement. If the temperature were measured optically using the laws for black body radiation, many of these limitations would be alleviated. Perhaps even more importantly, it would become possible to monitor thermal events in supported thin films with much greater sensitivity by virtue of the elimination of the thermocouple contact and thermal leakage.

The availability of high quality optical systems for the measurement and control of temperature encourages studies on the feasibility of an optical DTA. The following sections describe such a preliminary study and present encouraging initial results which do indeed clearly demonstrate the practicality of such instruments.

**EXPERIMENTAL PROCEDURES** - The optical thermometer marketed by the Luxtron Corporation was selected as the starting point. The Accufiber Model 100C has a dual sensor configuration that is ideal for this purpose. An example of the relative noise observed in such a system with that for a comparable noble metal thermocouple devise is shown in Fig. 1. The peak to peak noise observed is about 0.5 C for the thermocouple, but only 0.0002 C for the optical sensor. This suggests that the ultimate sensitivity obtainable from such an optical DTA will be determined by the ability to precisely program and control the temperature of the furnace.

Two single crystal light guides are provided with suitable polished surfaces. These were also used as the support system for the sample and reference crucibles as shown in Fig. 2. The proximity of the light guide to the sample is highly flexible based upon the optical systems used to focus the emission onto the opening of the light guide. For this initial venture the sample and reference crucibles were supported about 1 mm above the ends of the guides. The cool ends of these light pipes are coupled to optical fibers that conduct the signal to the measurement and control unit. Several crucibles were tried and alumina crucibles used in conventional DTA were found suitable. The undersides were coated with platinum black to provide a relatively good and reproducible black body emitter.

The control module coupled with the manufacturer's software converts the optical signals, derived from the radiant emission by the sample and reference, directly to temperature in accordance with Plank's law, equation 1, where \( E_b \) represents the energy emitted at the wavelength \( \lambda \) and temperature \( T \). \( C_1 \) and \( C_2 \) are constants. See reference 1 for further details.

\[
E_b(\lambda, T) = C_1 \lambda^{-5/2} \exp\left(\frac{C_2}{T}\right)^{-1}
\]

(1)
The value of $T$ is simply attained by subtracting the temperature of the reference from that of the sample. The temperature of the reference is also used to control the furnace temperature in accordance with the PID hardware and software supplied by the manufacturer.

Although the sensor is capable of measuring temperatures above 2000 °C, the alumina crucibles and supported rods limited the upper temperature of this initial system. Consequently a furnace capable of 1700 °C was selected. The furnace and its support system are essentially those of the Harrop high temperature DTA. The entire system is capable of operating in both oxidizing and reducing atmospheres at the rated temperature.

The system was calibrated using the melting point of gold. An emissivity value of 0.87 is used for an atmosphere of flowing argon (50 ml min$^{-1}$) and a heating rate of 20°C min$^{-1}$. This gave a value for the melting point of 1064 °C. The onset temperature was unchanged at a heating rate of 10 °C min$^{-1}$ as seen in Fig. 3. A reduced dependence of the observed temperature with variations in the heating rate is anticipated based on the improved thermal isolation of the sample and reference in an optically based system.

RESULTS AND DISCUSSION - As examples of first order phase transformations within the temperature range of this instrument, the melting of cobalt and the solid$\textsuperscript{1}$ to solid$\textsuperscript{2}$ (hexagonal to rhombohedral) transition in strontium carbonate were selected. The melting of cobalt had an onset temperature of about 1496 °C as can be seen in Fig. 4. The phase transformation for a sample during its second heating in carbon dioxide is shown in Fig. 5. The onset temperature for the reheat was at 934 °C, consistent with other work in carbon dioxide.$^{3,4}$

The ability to detect weak second order transformations was tested using the Curie temperature (ferromagnetic to paramagnetic transformation) for cobalt and the ferroelectric to paraelectric transformation in lithium niobate having the congruent melting composition.$^{5}$ These transitions do not have a change in enthalpy but only a change in the heat capacity. The resulting optical DTA curves are presented in Fig. 6. These very weak transitions can be detected satisfactorily.

CONCLUSIONS - These initial results clearly demonstrate not only the feasibility of an optical DTA but also indicate the high sensitivity and excellent accuracy that can be obtained from a properly calibrated instrument. Work is underway further demonstrate the usefulness of this approach to study transformations and reactions in thin films. The ability to sense the temperature of the surface rather than the bulk should markedly improve the usefulness of DTA to study supported thin films.
Figure 67. Noise comparison between a noble metal thermocouple and the optical fiber thermometer.

Figure 68. The optical DTA assembly with the accompanying furnace.
Figure 69. Melting of gold at 10°C/min. and 20°C/min.

Figure 70. Melting of cobalt in ODTA.
Figure 71. The hexagonal to rhombohedral transition in strontium carbonate.

Figure 72. Second order transition in cobalt and lithium niobate.
APPENDIX B

JCPDS Cards Used For Phase Identification
### Lithium Niobium Oxide

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<td>20</td>
<td>100</td>
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</tbody>
</table>

**Lamé**

- Rad. CuKα1 λ 1.5405 Filter Memo. Dia.
- Corriff 1/λ1 Diffractometer
- Ref. National Bureau of Standards, Mono. 25, Sec. 6, 22 (1968)

**Orthogonal**

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**Angles**

- αβγ > 2.00°
- Signs:
  - 2V
  - α
  - mp
  - Color Colorless

**Data**

- Ref. Ibid.

**Note:** The LiNbO₃ was obtained from CIBA, Rare Metals Division, Summit, New Jersey. Sample recrystallized at 950°C by W.S. Brower. It was pulled from a melt and then annealed in oxygen at 1100°C for 10 hours.

**Impurities:** 0.001-0.01% each: Na, K, Mg.
### Calcium Niobium Oxide

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* F$_2$/m (11) or F$_1$ (4)

### Lithium Niobate (V)

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* a = 8.433 b = 8.433 c = 8.433

### Ref.

- Rowland, Bright and Junge, Advances in X-ray Analysis, 2, 97-107 (1958)
- Blass, Z. anorg. allgem. Chem. 326, 44-46 (1963)
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**Silicon**

**Pattern at 2300°C.**

*Internal standard: K.*

*This sample is NBS Standard Reference Material 640.*

*d* is calculated from precision measurement of *d* <sub>9</sub>, *m* uncorrected for refraction.

*To replace 26-1481.*

### 6-0494

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**MgTiO₂**

**Magnesium Titanate** *(Geierlito)*

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**Colorless**

**Spect. anal. of sample 1: CO₂, 1% Al₂O₃, CaO**

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**Pattern at 2300°C.**

*Linear type structure*
REFERENCES


