THE STRUCTURAL AND OPTICAL PROPERTIES OF NEODYMIUM DOPED LITHIUM NIOBATE AND YTTRIUM ALUMINUM GARNET SINGLE CRYSTALS

NURUL WAHIDAH BINTI ZAINAL ABIDIN SHAM

UNIVERSITI TEKNOLOGI MALAYSIA
I dedicate this thesis to my lovely parents,
Zainal Abidin Sham Bin Musa and Marsitah Binti Samin;
My wonderful supervisor, family members and
all my friends who’s helping me throughout this thesis.
Thank you...
ACKNOWLEDGEMENT

I’m really grateful to Allah S.W.T for giving me the courage, strength and patience to complete this research.

I am heartily thankful to my supervisor, PM Dr. Md. Supar Bin Rohani, whose encouragement, guidance and support from the beginning to the end level enabled me to develop an understanding of the research and also to the entire Advanced Optical research Group (AOMRG) for their help on preparing the desired material for this project.

My grateful thanks also go to my family and friends. A big contribution and helped from all of you during this research was very great indeed. This research would be nothing without the enthusiasm and imagination from all of you.

My thanks also to MyBrain15 (MyMaster) and UTM for the financial support throughout this research study, which is really rewarding.
ABSTRACT

A Neodymium doped Lithium Niobate (LiNbO₃) single crystal of composition (48.6 - y) Li₂CO₃ + (51.4) Nb₂O₅ + (y) Nd₂O₃, (y = 0.5, y = 1.0) and a Neodymium doped Yttrium Aluminum Garnet (YAG) single crystal of composition (31 - y) Y₂O₃ + (69.0) Al₂O₃+ (y) Nd₂O₃, (y = 0.5, y = 1.0) were prepared by using Czochralski technique. The structural and optical properties of the crystals along the boule were investigated. The dopant concentration is varied along the crystal boule. The FTIR spectra of the Nd: LiNbO₃ crystals show that there are slight to the peaks at peaks of 3243 cm⁻¹ - 3251 cm⁻¹ when the content of Nd₂O₃ is increased and this shows the existence of OH bond stretching. In addition, the presence of the IR band in the range of 3567 cm⁻¹ - 3572 cm⁻¹ shows that the OH bond is due to the defect of the crystals while fundamental stretching of OH groups can be assigned to a band in the range of 3846 cm⁻¹ - 3866 cm⁻¹. As for the Nd: YAG crystals, sharp peaks are observed at 698 cm⁻¹ and 748 cm⁻¹ which can be assigned to Y – O symmetrical stretching and Y – O asymmetrical stretching, respectively. The first peak shifts slightly from 698 cm⁻¹ - 699 cm⁻¹ and the second peak from 748 cm⁻¹ - 751 cm⁻¹ as the content of Nd₂O₃ in the system is increased. In addition, a band in the range of 801 cm⁻¹ - 803 cm⁻¹ is assigned to Y – O bonds which have strong metal-oxygen stretching vibrations in tetrahedral arrangement. The IR peaks at 3290 cm⁻¹ - 3369 cm⁻¹ show the fundamental stretching of OH groups. The UV–Vis–NIR spectroscopy of Nd: LiNbO₃ crystals show that the values of indirect optical band gaps lie between 2.78 eV to 2.57 eV and those of the direct optical band gaps are between 3.82 eV to 3.71 eV. The Urbach energy for the Nd: LiNbO₃ crystal decreases from 0.69 eV to 0.48 eV. The UV–Vis–NIR spectroscopy of Nd: YAG crystals show that the values of indirect optical band gaps lie between 1.99 eV to 2.10 eV and those of the direct optical band gaps lie between 4.83 eV to 4.85 eV. The Urbach energy for the Nd: YAG crystal decreases from 2.44 eV to 2.09 eV. The change in band gaps is associated with the structural change occurring after the addition of Nd₂O₃ as the dopant in the crystal system. Luminescence spectra of Nd: LiNbO₃ crystals show that there is a ²G⁹/₂ → ⁴I⁹/₂ transition corresponding to a green emission at 492 nm and a ²H¹₁/₂ → ⁴I⁹/₂ transition corresponding to an orange emission at 621 nm. As for Nd: YAG crystals, there is a ²G¹₁/₂ → ⁴I⁹/₂ transition corresponding to a blue emission at 449 nm and a ²G⁹/₂ → ⁴I⁹/₂ transition corresponding to a cyan emission at 490 nm. As a conclusion, the two crystal systems show that the increase of Nd₂O₃ dopant from 0.5% mol to 1.0% mol will contribute to the decrease of crystal defects.
ABSTRAK

Satu hablur tunggal Lithium Niobate (LiNbO$_3$) didopkan Neodymium dengan komposisi (48.6 - y) Li$_2$CO$_3$ + (51.4) Nb$_2$O$_5$ + (y) Nd$_2$O$_3$, (y = 0.5, y = 1.0) dan satu hablur tunggal Yttrium Aluminum Garnet (YAG) didopkan Neodymium dengan komposisi (31 - y) Y$_2$O$_3$ + (69.0) Al$_2$O$_3$ + (y) Nd$_2$O$_3$, (y = 0.5, y = 1.0) telah disediakan menggunakan teknik Czochralski. Sifat struktur dan optik hablur di sepanjang jongkong dikaji. Komposisi dopan berbeza di sepanjang jongkong hablur. Spektrum FTIR bagi hablur Nd: LiNbO$_3$ menunjukkan terdapat sedikit perubahan pada puncak di 3243 cm$^{-1}$ - 3251 cm$^{-1}$ apabila kandungan Nd$_2$O$_3$ meningkat dan ini menunjukkan kehadiran ikatan OH. Tambahan lagi, jalur IR dalam julat 3567 cm$^{-1}$ - 3572 cm$^{-1}$ menunjukkan ikatan OH disebabkan oleh kecacatan hablur tersebut manakala regangan asas bagi kumpulan OH ditunjukkan pada jalur di dalam julat 3846 cm$^{-1}$ - 3866 cm$^{-1}$. Bagi hablur Nd:YAG, puncak tajam dapat dilihat pada 698 cm$^{-1}$ dan 748 cm$^{-1}$ yang maisng – masing merujuk kepada regangan simetri Y – O dan regangan tidak simetri Y – O. Puncak pertama beralih sedikit dari 698 cm$^{-1}$ - 699 cm$^{-1}$ dan puncak kedua dari 748 cm$^{-1}$ - 751 cm$^{-1}$ apabila kandungan Nd$_2$O$_3$ di dalam sistem bertambah. Tambahan lagi, jalur pada julat 801 cm$^{-1}$ - 803 cm$^{-1}$ menunjukkan ikatan Y – O yang mempunyai getaran regangan logam-oksigen yang kuat dalam susunan tetrahedral. Puncak IR pada 3290 cm$^{-1}$ - 3369 cm$^{-1}$ menunjukkan regangan asas kumpulan OH. Spektroskopi UV–Vis–NIR bagi hablur Nd: LiNbO$_3$, menunjukkan nilai jurang jalur optik tidak langsung terletak di antara 2.78 eV ke 2.57 eV dan jurang jalur optik langsung terletak di antara 3.82 eV ke 3.71 eV. Tenaga Urbach bagi hablur Nd: LiNbO$_3$ didapati menurun dari 0.69 eV ke 0.48 eV. Spektroskopi UV–Vis–NIR bagi hablur Nd: YAG menunjukkan nilai jurang jalur optik tidak langsung terletak di antara 1.99 eV ke 2.10 eV dan jurang jalur optik langsung terletak di antara 4.83 eV ke 4.85 eV. Tenaga Urbach bagi hablur Nd: YAG menurun dari 2.44 eV ke 2.09 eV. Perubahan di dalam jurang jalur adalah berkaitan dengan berlakunya perubahan struktur selepas penambahan Nd$_2$O$_3$ sebagai dopan di dalam sistem hablur. Spektrum luminesens bagi hablur Nd: LiNbO$_3$ menunjukkan terdapat transisi $^2$G$_{9/2}$ $\rightarrow$ $^4$I$_{9/2}$ merujuk kepada pancaran hijau pada 492 nm dan transisi $^2$H$_{11/2}$ $\rightarrow$ $^4$I$_{9/2}$ merujuk kepada pancaran oren pada 621 nm. Bagi hablur Nd: YAG,terdapat transisi $^2$G$_{11/2}$ $\rightarrow$ $^4$I$_{9/2}$ merujuk kepada pancaran biru pada 449 nm dan transisi $^2$G$_{9/2}$ $\rightarrow$ $^4$I$_{9/2}$ merujuk kepada pancaran sian pada 490 nm. Kesimpulannya, kedua-dua sistem hablur menunjukkan penambahan dopan Nd$_2$O$_3$ dari 0.5% mol ke 1.0% mol akan menyumbang kepada pengurangan kecacatan hablur.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
<td></td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iv</td>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>vi</td>
<td></td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vii</td>
<td></td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>viii</td>
<td></td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
<td></td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
<td></td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xvi</td>
<td></td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xviii</td>
<td></td>
</tr>
</tbody>
</table>

## 1 INTRODUCTION

1.1 Background Study 1
1.2 Problem Statement 6
1.3 Objectives 7
1.4 Scope 8
1.5 Thesis Overview 8

## 2 LITERATURE REVIEW

2.1 Introduction 9
2.2 Crystal Growth and Czochralski (Cz) Technique 10
2.3 Working Principle For Czochralski Technique 11
2.4 Morphology of Single Crystals 15
2.5 Lithium Niobate 16
  2.5.1 Crystallographic Properties of Lithium Niobate 18
  2.5.2 Linear and Nonlinear optical properties of Lithium
          Niobate 21
2.6 Yttrium Aluminum Garnet 22
2.7 Neodymium 26
  2.7.1 Neodymium doped Lithium Niobate single crystal 29
  2.7.2 Neodymium doped Yttrium Aluminum Garnet
           single crystal 30
2.8 FTIR Spectroscopy 33
  2.8.1 IR Spectroscopy 34
2.9 UV – Vis – NIR Spectroscopy 38
  2.9.1 Absorption 39
  2.9.2 Interband Optical Absorption 43
  2.9.3 General Distinction of Direct and Indirect Band Gap 45
2.10 Photoluminescence 47
  2.10.1 Upconversion Process 48
  2.10.2 Excited State Absorption (ESA) 49
  2.10.3 Photon Avalanche (PA) 50
  2.10.4 Energy Transfer Upconversion (ETU) 51

3  RESEARCH METHODOLOGY 53
3.1 Introduction 53
3.2 Sample Preparation 54
  3.2.1 Czochralski Furnace Set Up 55
  3.2.2 Crystal Growth Process 57
  3.2.3 Cutting and Polishing Process 57
3.3 Spectroscopic Analysis 58
  3.3.1 UV – Visible Spectroscopy Technique 58
  3.3.2 Optical Band Gap Energy (Eg) 60
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Physical properties of Lithium Niobate (Prokhorov et.al., 1990).</td>
<td>21</td>
</tr>
<tr>
<td>2.2</td>
<td>Yttrium Aluminum Garnet (YAG) material properties (Powell, 1989).</td>
<td>25</td>
</tr>
<tr>
<td>2.3</td>
<td>Material Properties of Nd:YAG crystal (Product Brochure of VLOC, 1999).</td>
<td>33</td>
</tr>
<tr>
<td>2.4</td>
<td>Classification of infrared radiation.</td>
<td>34</td>
</tr>
<tr>
<td>2.5</td>
<td>Types of vibration mode of molecules (Division of Chemistry Homepage, 2004).</td>
<td>37</td>
</tr>
<tr>
<td>4.1</td>
<td>Composition and appearance of Nd: LiNbO$_3$.</td>
<td>66</td>
</tr>
<tr>
<td>4.2</td>
<td>Composition and appearance of Nd: YAG.</td>
<td>66</td>
</tr>
<tr>
<td>4.3</td>
<td>The FTIR peaks positions of Nd: LiNbO$_3$ crystals.</td>
<td>68</td>
</tr>
<tr>
<td>4.4</td>
<td>Band positions (in cm$^{-1}$) of FTIR spectra of Nd: LiNbO$_3$ crystals.</td>
<td>69</td>
</tr>
<tr>
<td>4.5</td>
<td>The FTIR peaks positions of Nd: YAG crystals.</td>
<td>71</td>
</tr>
<tr>
<td>4.6</td>
<td>Band positions (in cm$^{-1}$) of FTIR spectra of Nd: YAG crystals.</td>
<td>72</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>Calculated Optical Band Gap ($E_{\text{opt}}$) and Urbach Energy ($E_{\text{tail}}$) of Nd: LiNbO$_3$ crystal.</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>Calculated Optical Band Gap ($E_{\text{opt}}$) and Urbach Energy ($E_{\text{tail}}$) of Nd: YAG crystal.</td>
<td></td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Czochralski Crystal Growth Process (Tomaszewski, 2002).</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>Flow process of the Czochralski technique.</td>
<td>13</td>
</tr>
<tr>
<td>2.3</td>
<td>Overall process of crystal growth using CZ technique (Hamdan, 2007).</td>
<td>14</td>
</tr>
<tr>
<td>2.4</td>
<td>Phase diagram of Li$_2$O-Nb$_2$O$_2$ (Malovichko et al., 2001).</td>
<td>17</td>
</tr>
<tr>
<td>2.5</td>
<td>Typical example of growth pure Lithium Niobate crystal.</td>
<td>18</td>
</tr>
<tr>
<td>2.6</td>
<td>Diagram of Lithium Niobate crystal structure in A) Ferroelectric phase and B) Paraelectric phase (Weis et al., 1985).</td>
<td>19</td>
</tr>
<tr>
<td>2.7</td>
<td>Miller indices of Lithium Niobate.</td>
<td>20</td>
</tr>
<tr>
<td>2.8</td>
<td>Graph of ordinary and extraordinary refractive index of Lithium Niobate with wavelength within its optical transmission range (Edwards et al., 1984).</td>
<td>22</td>
</tr>
<tr>
<td>2.9</td>
<td>A unit cell of YAG crystal. A) Blue, grey and red sites are occupied by yttrium, aluminum and oxygen respectively. All together, the unit cell contains eight molecular units Y$_3$Al$<em>5$O$</em>{12}$. B) The local surrounding of one yttrium site (Kolesov R. et al., 2012).</td>
<td>24</td>
</tr>
</tbody>
</table>
2.10 Typical example of Nd:YAG laser rod, diameter 0.5 cm.  
2.11 Energy levels of Nd$^{3+}$ ions in crystals (Norshafadzila, 2012).  
2.12 Graph of Neodymium concentration vs fraction of melt pulled (Product Brochure of VLOC, 1999).  
2.13 Graph of Neodymium concentrations versus net boule length (Product Brochure of VLOC, 1999).  
2.14 Energy diagram of two separated bands in solid (Mark, 2010).  
2.15 Schematic diagram for direct band gap in solids.  
2.16 Schematic diagram for indirect band gap in solids.  
2.17 Schematic diagram of ESA.  
2.18 Schematic diagram of photon avalanche process.  
2.19 Energy transfer processes between two ions: (a) resonant non radiative transfer; (b) phonon assisted non radiative transfer. (S: sensitizer ions, A: activator ions) (Auzel, 2004).  
3.1 Flow chart of the sample preparation and characterization.  
3.2 Schematic diagram of furnace external setup (Hamdan, 2007).  
3.3 Insulation setup in furnace.  
3.4 Working principle of UV-Vis-NIR Spectroscopy.  
3.5 Working principle of Photoluminescence Spectroscopy.  
3.6 Layout of FTIR Spectroscopy.  
4.1 Infrared transmission spectra of Nd: LiNbO$_3$.  

26  
28  
31  
32  
43  
46  
46  
49  
50  
52  
54  
56  
56  
59  
62  
64  
68
4.2 Infrared transmission spectra of Nd: YAG.

4.3 Typical UV-Vis-NIR absorption spectra of Nd: LiNbO$_3$ crystal.

4.4 A typical graph of $(\alpha \hbar \omega)^{1/2}$ vs $\hbar \omega$ of Nd: LiNbO$_3$ crystal.

4.5 A typical graph of $(\alpha \hbar \omega)^2$ vs $\hbar \omega$ of Nd: LiNbO$_3$ crystal.

4.6 A typical graph of $\ln \alpha$ vs $\hbar \omega$ of Nd: LiNbO$_3$ crystal.

4.7 Typical UV-Vis-NIR absorption spectra of Nd: YAG crystal.

4.8 A typical graph of $(\alpha \hbar \omega)^{1/2}$ vs $\hbar \omega$ of Nd: YAG crystal.

4.9 A typical graph of $(\alpha \hbar \omega)^2$ vs $\hbar \omega$ of Nd: YAG crystal.

4.10 A typical graph of $\ln \alpha$ vs $\hbar \omega$ of Nd: YAG crystal.

4.11 Typical luminescence spectra of Li$_2$CO$_3$ + Nb$_2$O$_5$ + Nd$_2$O$_3$ system under 585 nm excitation at room temperature.

4.12 Energy level schemes of Nd$^{3+}$ with relative transitions of Lithium Niobate crystals system.

4.13 Typical luminescence spectra of Y$_2$O$_3$ + Al$_2$O$_3$ + Nd$_2$O$_3$ system under 585 nm excitation at room temperature.

4.14 Energy level schemes of Nd$^{3+}$ with relative transitions of YAG crystals system.
LIST OF SYMBOLS

\( \alpha (v) \) - Urbach function
\( \alpha \) - absorption coefficient
\( a \omega \) - fundamental of absorption edge
\( \Delta E \) - width of band tails of localized states
\( \lambda \) - wavelength
\( \omega \) - frequency dependence
\( h\omega/ h \nu \) - photon energy
\( \mu \) - reduced mass of cation – anion molecules
\( A \) - absorption intensity
\( B \) - constant
\( \text{BO} \) - bridging oxygen
\( c \) - speed of light
\( \text{CB} \) - conduction band
\( \text{CR} \) - cross relaxation
\( d \) - thickness of crystal
\( d \) - the plane parallel sample thickness
\( E_f \) - final state of energy
\( E_g \) - optical band gap
\( E_i \) - initial state of energy
\( E_{\text{opt}} \) - optical band gap
\( \text{ESA} \) - excited state absorption
ETU - energy transfer upconversion

eq - equatorial

f - force constant

FTIR - Fourier Transform Infrared

h - Planck’s constant

IR - infrared

k - momentum

Li₂CO₃ - Lithium carbonate

mₒ - atomic weight of cation o

mᵣ - atomic weight of cation r

n - integer

Nb₂O₅ - Niobium pentoxide

Nd₂O₃ - Neodymium (III) oxide

NIR - near infrared

p - index characterize of optical absorption process

q - phonon

Tₖ - crystallization temperature

T - the transmittance

UV - ultraviolet

V - specific volume

v - frequency of incident photons

k - wave number

VB - valence band

Vis - visible
## LIST OF APPENDIX

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>FTIR Spectra of Nd: LiNbO$_3$ and Nd:YAG</td>
<td>105</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Background Study

A crystal can be defined as a solid material whose being a part of whole atoms, molecules or ions that arranged in an orderly repeating pattern extending in all three spatial dimension while the crystal growth is a major stage of a crystallization process and consists in the addition of new atoms, ions or polymer strings into the characteristic arrangement of a crystalline Bravais lattice. It is also a homogenous anisotropic substance where the physical properties such as refractive index, electrical conductivity and magnetic conductivity have different directions which is definite geometrical shape with surface that are usually plane and sharp edges (Gurtu et.al., 1970). The crystals structure is a time-invariant, three dimensional (3-D) arrangements of atoms or molecules on a lattice (Graef et.al., 2007). As the temperature decrease below the freezing point, the kinetic energy becomes small that the molecules become permanently attached to one another. In addition, the movement of the molecules in crystal consist only vibrations about the central position (Walter Borchardt-Ott, 1993).
Nowadays, the world crystal production is estimated at more than 20,000 tons per year, of which the largest fraction of about 60% are semiconductors silicon, GaAs, InP, GaP, CdTe and its alloys. This scale of crystal production and the fact that most crystals are produced in factories specialized in silicon or Gallium Arsenide (GaAs) or Lithium Niobate (LiNbO$_3$) has caused an increasing degree of specialization (Scheel, 2000). Furthermore, crystals are produced artificially today to satisfy the desire of science, technology and jewellery industry. The most important thing is the ability to grow a high quality of crystals nowadays has become an intense competition all around the world.

Lithium Niobate, LiNbO$_3$ crystal is well known for its remarkable physical properties, such as electro-optical, acousto-optical and non-linear optical properties which lead to wide technical applications and fundamental research. Pure LiNbO$_3$ and doped LiNbO$_3$ crystals are widely used for holographic data storage, frequency doubling, waveguide structures and solid state lasers (Yang et al., 2002). It is manmade, naturally birefringent, ferroelectric material with large pyroelectric, piezoelectric, electro-optic and photo elastic coefficients. It is also exhibits very strong bulk photovoltaic and photorefractive effects. Worldwide production exceeds five tons per annum making it second largest volume manmade crystal after silicon (Prokhorov et al., 1990).

The advantage of using LiNbO$_3$ crystalline host is it can also produce higher absorption and emission cross-sections than amorphous glass and doping it with foreign ions modifies the optical properties of the matrix and makes the system useful for a great variety of those applications (Qiang et al., 2002). One of the potential application of LiNbO$_3$ is in Nd$^{3+}$ -based compact diode-pumped self frequency double lasers which emit green radiation, useful for applications in undersea imaging, optical data storage and excitation sources to replace ion gas lasers for science and pumping of parametric oscillators and amplifiers (Norshafadzila, 2012). Nd doped LiNbO$_3$ is also well known, multi used, easy to grow and structurally simplest laser materials.
Yttrium Aluminum Garnet \( \text{Y}_3\text{Al}_5\text{O}_{12} \) (YAG) single crystal is widely used for laser materials and other luminous matrix materials due to its excellent optical properties (Xudong et.al., 2013) and it is one of the hardest and most durable materials. Pure YAG crystal has a good transmission from ultraviolet (UV) to infrared (IR), high chemical resistance and high thermal conductivity. It is also one of the most important photonic materials with a wide range of lasers, optoelectronics and scintillation. The optical properties of garnets are strongly related with the excitation dynamics and defects in the structure. Characterization and identification of the electron and hole traps are essential to understand excitation dynamics and thus, control the optical properties (Varney et.al., 2012 a).

The rare earth ion doped materials which has low cutoff phonon energy, have received great importance recently due to their wide range of applications in lasers, optical amplifiers and optical sensors among other devices (Li et.al., 2010). They are also categorized as a special material due to their excellent optical properties, chemical durability and also thermal stability. One of the widely used rare earth element is Neodymium. Neodymium is a soft, malleable, ductile, reflective grey metal that easily oxidizes in both air and water, and it is found in the +3, +2 and +4 oxidation states (Hoatson et.al., 2011). Neodymium-doped crystals generate high-powered infrared laser beams which are converted to green laser light in commercial diode pumped solid state laser hand-held lasers and laser pointers. Neodymium also has been used for plant growth fertilizer and determining the age relationships of rocks and meteorites.

The distribution of dopant ions in the lattice matrix of a host single crystal depends on the concentration, size and ionic state of dopant and these incorporate homogeneously in the lattice only up to a certain concentration or threshold concentration. Above the threshold concentration, high geometric strain develops in the lattice and tries to attain a relaxed state. During this process, dynamics of point defects take place leading to agglomeration of point defects, dislocations and even the formation
of structural grain boundaries. The properties of single crystals are anisotropic in nature and in the presence of structural defects these get masked or partially deteriorate and thereby reduce the efficiency of the device property. Therefore, for realization of full efficiency of the devices, the crystal must be free from such structural defects. In the modern era of miniaturized technology of photonic devices it is very important to grow bulk single crystals and assess their crystalline perfection especially in the case of doped crystals (Kushwaha et.al., 2012).

Combining the LN and YAG host properties with spectroscopic properties of dopant, higher component integration may be achieved. In addition, the material and optical properties of the crystal are also changed by the amount and type of dopant added. Therefore, suitable dopant types and concentration can be select based on desired application. The efficiency of the rare earth elements depends partly on the excited state lifetime of the ions, which strongly depends on the local environment.

Neodymium (Nd) doped Yttrium Aluminum Garnet (YAG) crystal possessed as one of the important laser hosts generation of 1.06 μ infra-red radiation (Norshafadzila, 2012). The garnet host is a cubic crystal with space group Ia3d. It has high mechanical strength, good chemical stability and the ability to be synthesized in large sizes with high optical quality (Powell, 1998). Nd:YAG crystal also known as one of the most widely used solid state laser material adopted by industrial, scientific and medical. Advantages of using Nd:YAG are low threshold, high gain, high efficiency, good thermal shock characteristics and thermal conductivity, mechanical strength, high optical quality and material characteristics that allow for various modes of operation such as mode locked, Q-switched and cavity dumped modes of operation. The goal for commercial suppliers of Nd:YAG is to grow highly doped, large diameter crystals. Increasing the Neodymium Nd$^{3+}$ dopant concentration will results in a higher absorption coefficient, lower fluorescence life-time and improves the overall laser efficiency.
However, raising Neodymium concentration also increases the frequency of cracking during growth process (Jiang et. al., 2006).

Lithium Niobate, LiNbO$_3$ (LN) single crystals have been widely used because of their good electro-optic and non-linear properties. Others effects are also being exploited, such as the strain-optic effect to implement wavelength- tunable polarization converters (Liangsheng et. al., 2002). In recent years there has been an increasing interest for massive or local doping of LN in order to extend its functionality. Moreover, doping with damage resistant dopant is found to be an effective method to increase the optical damage resistance where the elements are Zn (Xi- He et. al., 2003; Xi- He et. al., 2005), Mg (Liangsheng et. al., 2002), In (Kong et. al., 1995) and Sc (Yamamoto et. al., 1992). Lithium Niobate crystals doped with rare-earth (RE) ions such as Er (Bermudez et. al., 1999; Sosa et. al., 2005), Nd (Sokolska et. al., 1999), Ce (Wang et. al., 2009) and Yb (Huang et. al., 2005) will exhibits a combination of active (laser) and nonlinear properties (“active- nonlinear” crystals) and it had been investigated intensively during the last decade (Palatnikov et. al., 2006). Neodymium (Nd) doped Lithium Niobate (LiNbO$_3$) is based compact diode-pumped self frequency double lasers which emit green radiation is useful for applications in optical data storage and undersea imaging (Capmany et. al., 1999). The development of solid state frequency up converters based upon rare earth doped Lithium Niobate hosts has attracted a great deal of technological and scientific interest lately. The rare earth doped solid state up converter can find applications in photonic devices including sensors, up conversion lasers and compact lasers due to the possibility of second harmonic generation by quasi-phase matching and of using more complicated frequency conversion processes such as frequency subtraction and addition (Li et. al., 2010).

Lithium Niobate and Yttrium Aluminum Garnet single crystals were grown by the Czochralski in air environment using the automatic diameter control setup. There are other crystal growth technique such as Verneuil, flux, Bridgman (Li et. al., 2011) and
Stepanov. This Czochralski method was used because it can controlled the diameter and size of grown crystals during the growth of the crystals. The Czochralski method is the most common technique for growing bulk LN single crystal from a congruent melt composition (Chiang and Chen, 2006) without defects and dislocation. However, to growth a defects free crystal is still a secret to the company and researcher. The Czochralski method had been used by many researchers in previous studies (Dominiak-Dzik et.al., 1994; Yi Lu et.al., 2003; Zhen et.al., 2003).

1.2 Problem Statement

The study of crystal growth nowadays relates to the need of technology for preparing better and efficient Lithium Niobate and Yttrium Aluminum Garnet crystals with controlled dopant. The study of Nd: LiNbO$_3$ and Nd:YAG crystals which emphasized on the spectroscopic properties has previously been done by many researchers. Doping Lithium Niobate with foreign ions modifies the optical properties of the matrix and makes the system useful for a variety of applications such as solid state lasers, optical waveguides and photorefractive device (Armenise et.al., 1983). The Neodymium doped Y$_3$Al$_5$O$_{12}$ (Nd:YAG) crystals are widely used as the pumping medium in solid state lasers and the garnet host has high mechanical strength, good chemical stability and the ability to synthesized in large sizes with high optical quality. However, the differentiation between these two different doped crystals is not fully unrevealed. Therefore, the aims for this research are to study the difference of spectroscopic properties on optical and structural of the doped crystals where the characterization of absorption spectra will contribute the value of energy band gap and Urbach energy while photoluminescence will produce the up conversion spectra. In addition, based on previous research, there are many experiment done on Nd:YAG crystal growth rather than Nd: LiNbO$_3$. Therefore, the characteristic of Nd: LiNbO$_3$
crystal can be improved based on the comparison between these two systems where Nd: YAG possessed good characteristics used in application of laser. Moreover, the Czochralski technique enhanced with automatic diameter controller crystal growth system (ADC-CGS) is used for growing the Nd: LiNbO₃ and Nd:YAG single crystals.

1.3 Objectives

1) To investigate the crystal growth process of Nd: LiNbO₃ and Nd:YAG crystal by using Czochralski technique.

2) To investigate the role of Neodymium in LiNbO₃ and YAG single crystals.

3) To characterize the optical and structural properties of Nd: LiNbO₃ and Nd:YAG single crystals by using UV-Visible, Photoluminescence and Fourier Transform Infrared spectroscopic techniques.

4) To differentiate the structural and optical properties between the two doped crystal systems.
1.4 Scope

Research that have been conducted consist of preparation of a series of Neodymium doped Lithium Niobate and Yttrium Aluminum Garnet single crystals using automatic diameter control techniques by Czochralski crystal growth method. UV-visible, photoluminescence and Fourier Transform Infrared (FTIR) spectroscopy technique are used to characterize the optical and structural properties of the crystals. The differences between these two doped crystals are determined and discussed.

1.5 Thesis Overview

Chapter 1 is an introduction of the background study on growth of single crystal. There are definition and properties of crystals, crystal growth method, properties of Lithium Niobate single crystal and Yttrium Aluminum Garnet single crystal. Chapter 2 provides the general basic of Cz method which include working principle, preparation of materials, general structure of Lithium Niobate single crystal and Yttrium Aluminum Garnet single crystal. Moreover, there are also details about spectroscopic techniques which are UV-Visible, Photoluminescence and Fourier Transform Infrared (FTIR). Chapter 3 describes the research methodology by using spectroscopic techniques and Chapter 4 provides the results obtained from the experiment and contributes to the discussion and differentiation between both samples. The conclusion and recommendation for further study are discussed in Chapter 5.
REFERENCES


