

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

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*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...*

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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 ²G_{9/2} → ⁴I_{9/2} transition corresponding to a green emission at 492 nm and a ²H_{11/2} → ⁴I_{9/2} transition corresponding to an orange emission at 621 nm. As for Nd: YAG crystals, there is a ²G_{11/2} → ⁴I_{9/2} transition corresponding to a blue emission at 449 nm and a ²G_{9/2} → ⁴I_{9/2} 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 $(48.6 - y) \text{Li}_2\text{CO}_3 + (51.4) \text{Nb}_2\text{O}_5 + (y) \text{Nd}_2\text{O}_3$, ($y = 0.5, y = 1.0$) dan satu hablur tunggal Yttrium Aluminum Garnet (YAG) didopkan Neodymium dengan komposisi $(31 - y) \text{Y}_2\text{O}_3 + (69.0) \text{Al}_2\text{O}_3 + (y) \text{Nd}_2\text{O}_3$, ($y = 0.5, y = 1.0$) 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 $3243 \text{ cm}^{-1} - 3251 \text{ cm}^{-1}$ apabila kandungan Nd_2O_3 meningkat dan ini menunjukkan kehadiran ikatan regangan OH. Tambahan lagi, jalur IR dalam julat $3567 \text{ cm}^{-1} - 3572 \text{ cm}^{-1}$ menunjukkan ikatan OH disebabkan oleh kecacatan hablur tersebut manakala regangan asas bagi kumpulan OH ditunjukkan pada jalur di dalam julat $3846 \text{ cm}^{-1} - 3866 \text{ cm}^{-1}$. Bagi hablur Nd:YAG, puncak tajam dapat dilihat pada 698 cm^{-1} dan 748 cm^{-1} yang masing – masing merujuk kepada regangan simetri Y – O dan regangan tidak simetri Y – O. Puncak pertama beralih sedikit dari $698 \text{ cm}^{-1} - 699 \text{ cm}^{-1}$ dan puncak kedua dari $748 \text{ cm}^{-1} - 751 \text{ cm}^{-1}$ apabila kandungan Nd_2O_3 di dalam sistem bertambah. Tambahan lagi, jalur pada julat $801 \text{ cm}^{-1} - 803 \text{ cm}^{-1}$ menunjukkan ikatan Y – O yang mempunyai getaran regangan logam-oksigen yang kuat dalam susunan tetrahedral. Puncak IR pada $3290 \text{ cm}^{-1} - 3369 \text{ cm}^{-1}$ 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_2O_3 sebagai dopan di dalam sistem hablur. Spektrum luminesens bagi hablur Nd: LiNbO_3 menunjukkan terdapat transisi ${}^2\text{G}_{9/2} \rightarrow {}^4\text{I}_{9/2}$ merujuk kepada pancaran hijau pada 492 nm dan transisi ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{9/2}$ merujuk kepada pancaran oren pada 621 nm. Bagi hablur Nd: YAG, terdapat transisi ${}^2\text{G}_{11/2} \rightarrow {}^4\text{I}_{9/2}$ merujuk kepada pancaran biru pada 449 nm dan transisi ${}^2\text{G}_{9/2} \rightarrow {}^4\text{I}_{9/2}$ merujuk kepada pancaran sian pada 490 nm. Kesimpulannya, kedua-dua sistem hablur menunjukkan penambahan dopan Nd_2O_3 dari 0.5% mol ke 1.0% mol akan menyumbang kepada pengurangan kecacatan hablur.

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LIST OF SYMBOLS

$\alpha(\nu)$	- Urbach function
α	- absorption coefficient
$\alpha\omega$	- fundamental of absorption edge
ΔE	- width of band tails of localized states
λ	- wavelength
ω	- frequency dependence
$\hbar\omega/h\nu$	- photon energy
μ	- reduced mass of cation – anion molecules
A	- absorption intensity
B	- constant
BO	- bridging oxygen
c	- speed of light
CB	- conduction band
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_{opt}	- optical band gap
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
Li_2CO_3	- Lithium carbonate
m_o	- atomic weight of cation o
m_r	- atomic weight of cation r
n	- integer
Nb_2O_5	- Niobium pentoxide
Nd_2O_3	- Neodymium (III) oxide
NIR	- near infrared
p	- index characterize of optical absorption process
q	- phonon
T_c	- crystallization temperature
T	- the transmittance
UV	- ultraviolet
V	- specific volume
ν	- frequency of incident photons
k	- wave number
VB	- valence band
Vis	- visible

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CHAPTER 1

INTRODUCTION

1.1 Background Study

A crystal can be define 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 $Y_3Al_5O_{12}$ (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 Nd³⁺ 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: LiNbO₃ 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 Y₃Al₅O₁₂ (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: LiNbO₃. Therefore, the characteristic of Nd: LiNbO₃

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.

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