STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF UNSTRAINED AND STRAINED $LiNbO_3$: A FIRST-PRINCIPLES STUDY

ROSLAN BIN HUSIN

MASTER OF SCIENCE (PHYSICS)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

2021

STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF UNSTRAINED AND STRAINED $LiNbO_3$: A FIRST-PRINCIPLES STUDY

ROSLAN BIN HUSIN

Thesis submitted to the Centre for Graduate Studies, Universiti Pertahanan Nasional Malaysia, in fulfilment of the requirements for the Degree of Master of Science (Physics)

January 2021

ABSTRACT

The exchange-correlation functions of local density approximation and generalized gradient approximation using density functional theory were performed to calculate electronic and optical properties of $LiNbO_3$ crystal. To improve the underestimated value of band gap, a reverse scissor correction procedure was performed based on the experimental refractive index value because it is more suitable for compound with polar crystal. It is found that underestimated electronic band gap ~4.76 eV was generated due to nature of generalized gradient approximation exchange correlation. Based on density of states calculation, Li ion tends to diffuse into substrate as it possesses pure ionic character. Thus, the chemical bonding in $LiNbO_3$ crystal has a mixed covalent-ionic character. The effect of strain on *a*-axis and *c*-axis of the crystal toward electronic and optical properties were investigated. It is found that the *a*-axis of the crystal is more sensitive towards the strain compared to *c*-axis as the band gap largely changes upon the applied strain. The optical properties such as dielectric function, refractive index, extinction coefficient and absorption were calculated and explained in detail. The dielectric constant and refractive index increased to higher frequency with positive strain and vice versa. Meanwhile for the absorption decreased to lower frequency with positive strain and vice versa. These results would assist to provide the fundamental explanation about the effect of strain on the properties of $LiNbO_3$ crystal.

ABSTRAK

Fungsi pertukaran korelasi bagi penghampiran ketumpatan tempatan dan penghampiran kecerunan umum berdasarkan teori fungsi ketumpatan digunakan untuk mengira sifat elektronik dan optik kristal $LiNbO_3$. Untuk membetulkan nilai yang kurang tepat dari jurang jalur, kaedah pembetulan gunting terbalik dilakukan berdasarkan nilai indek biasan eksperimen kerana ia lebih sesuai untuk sebatian dengan kristal yang berkutub. Didapati bahawa jurang jalur elektronik yang kurang tepat ~4.76 eV adalah disebabkan sifat semulajadi penghampiran kecerunan umum dari fungsi pertukaran korelasi. Berdasarkan pegiraan ketumpatan keadaan, ion Li cenderung meresap ke dalam substrat kerana ia mempunyai sifat ionik tulen. Oleh itu, ikatan kimia dalam kristal $LiNbO_3$ mempunyai campuran watak ion-kovalen. Kesan ketegangan pada paksi-*a* dan paksi-*c* pada kristal terhadap sifat elektronik dan optik disiasat. Didapati bahawa paksi-*a* adalah lebih sensitif terhadap ketegangan berbanding paksi-*c* disebabkan sebahagian besar jurang jalur berubah apabila ketegangan dikenakan. Sifat optik seperti fungsi dielektrik, indeks biasan, pekali kepupusan dan penyerapan akan dikira dan dijelaskan secara terperinci. Indeks pemalar dan biasan dielektrik akan meningkat kepada frekuensi yang lebih tinggi terhadap ketegangan positif atau sebaliknya. Manakala untuk penyerapan menurun ke frekuensi lebih rendah terhadap ketegangan positif atau sebaliknya. Hasilnya, ia akan memberi penjelasan asas mengenai kesan ketegangan pada sifat kristal LiNbO3.

ACKNOWLEDGEMENTS

Alhamdulillah, first and foremost, praises and thanks to Allah S.W.T, for endless blessings, giving me an opportunity to study in Universiti Pertahanan Nasional Malaysia (UPNM). I would like to express my deep and sincere gratitude to my research supervisor, Lt Kol Prof. Ts. Dr. Muhd Zu Azhan bin Yahya for giving me the opportunity to do research under his supervisions and providing me invaluable guidance throughout this research. His dynamism, vision and sincerity and motivation have deeply inspired me. I am extremely grateful for what he has offered me. I am extending my heartfelt thanks to my co-supervisors, Dr. Fadhlul Wafi bin Badrudin and Dr. Mohd Fariz bin Mohmad Taib for their continuous support to guide my study research, for their patience, motivation, enthusiasms and immense knowledge. Their guidance help me in accomplishing this research and writing the thesis.

I am extremely grateful to my parents for their love, prayers, caring and sacrifice for educating me and preparing me for my future. I am very much thankful to my lovely wife, Nur Faieza binti Mohd Amin and my kids, Muhammad Faheem Danial, Muhammad Qhaleef Dayyan, Muhammad Reezqi Daris and Muhammad Ghazee Dahin for their love, understanding, prayers, giving motivation and spiritual support and even fully taking care of me during difficult times and hardship.

Besides, I would like to thank members of the computational group-imade UiTM, Assoc. Prof. Dr. Ing Oskar, Dr. Hafiz, Dr. Hezrie and other colleagues for their continuous support. Last but not least, I wish to express my sincere thanks to those who have directly or indirectly for helped me in making this study success.

APPROVAL

The Examination Committee has met on **10th November 2020** to conduct the final examination of **Roslan bin Husin** on his degree thesis entitled 'Structural, Electronic and Optical Properties of Unstrained and Strained $LiNbO_3$: A First-Principles Study'. The committee recommends that the student be awarded the Master of Science (Physics).

Members of the Examination Committee were as follows.

Assoc. Prof. Dr. Norhana binti Abdul Halim
Center for Defence Foundation
Universiti Pertahanan Nasional Malaysia
(Chairman)

Dr. Muhammad Faiz bin Md Din
Faculty of Engineering
Universiti Pertahanan Nasional Malaysia
(Internal Examiner)

Prof. Dr. Ab Malik bin Marwan
Faculty of Applied Sciences
University Technology MARA
(External Examiner)

APPROVAL

This thesis was submitted to the Senate of Universiti Pertahanan Nasional Malaysia and has been accepted as fulfilment of the requirements for the degree of **Master of Science (Physics)**. The members of the Supervisory Committee were as follows.

Lt Col Prof. Ts. Dr. Muhd Zu Azhan bin Yahya
Deputy Vice Chancellor (Students Affairs & Alumni)
Universiti Pertahanan Nasional Malaysia
(Main Supervisor)

Dr. Fadhlul Wafi bin Badrudin
Faculty of Defence Science and Technology
Universiti Pertahanan Nasional Malaysia
(Co-supervisor)

Dr. Mohamad Fariz bin Mohamad Taib
Faculty of Applied Sciences
Universiti Teknologi MARA
(Co-supervisor)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

DECLARATION OF THESIS

Student's full name : Roslan bin Husin
Date of birth : 9th July 1981
Title : Structural, Electronic and Optical Properties of Unstrained and Strained $LiNbO_3$: A First-Principles Study
Academic session : 2020/2021

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged.

I further declare that this thesis is classified as:

☐ **CONFIDENTIAL** (Contains confidential information under the official Secret Act 1972)*

☐ **RESTRICTED** (Contains restricted information as specified by the organisation where research was done)*

☐ **OPEN ACCESS** I agree that my thesis to be published as online open access (full text)

I acknowledge that Universiti Pertahanan Nasional Malaysia reserves the right as follows.

1. The thesis is the property of Universiti Pertahanan Nasional Malaysia.
2. The library of Universiti Pertahanan Nasional Malaysia has the right to make copies for the purpose of research only.
3. The library has the right to make copies of the thesis for academic exchange.

Signature	Signature of Main Supervisor/Dean of CGS/Chief Librarian
810709-01-5555	Lt Kol Prof. Ts Dr. Muhd Zu Azhan bin Yahya
IC/Passport No.	Name of Main Supervisor/Dean of CGS/Chief Librarian
Date:	Date:

Note: *If the thesis is CONFIDENTAL OR RESTRICTED, please attach the letter from the organisation stating the period and reasons for confidentiality and restriction.23

TABLE OF CONTENTS

		Page
ABSTRACT		ii
ABSTRAK		iii
ACKNOWLEDGEMENTS		iv
APPROVAL		v
DECLARATION		vii
TABLE OF CONTENTS		viii
LIST OF TABLES		x
LIST OF FIGURES		xi
LIST OF ABBREVIATIONS		xiii
CHAPTER		
1	**INTRODUCTION**	1
	1.1 Background	1
	1.2 Problem Statement	2
	1.3 Objectives	3
	1.4 Significance or Research	3
	1.5 Scope and Limitation of Research	4
	1.6 Thesis Outline	5
2	**LITERATURE REVIEW**	6
	2.1 Introduction	6
	2.2 Ferroelectric Materials	6
	2.3 Lithium Niobate	9
	2.4 Structural Properties of $LiNbO_3$	11
	2.5 Electronic Properties of $LiNbO_3$	12
	2.6 Optical Properties of $LiNbO_3$	13
	2.7 Strain Effect	15
	2.8 Summary of Chapter	19
3	**COMPUTATIONAL METHOD**	20
	3.1 Introduction	20
	3.2 First-Principles Study	20
	3.3 Density Function Theory	21
	3.4 Exchange-Correlation Functional	22
	3.4.1 Local Density Approximation (LDA)	22
	3.4.2 Generalized Gradient Approximation (GGA)	22
	3.5 Cambridge Serial Total Energy Package (CASTEP)	23
	3.6 Computational Method	25
	3.6.1 Modelling of Crystal Structure	26
	3.6.2 Structural Optimization	27
	3.6.3 Electronic and Optical Properties Calculation	28
	3.6.4 Data Analysis	30

3.7 Applied Theory in Analyzing $LiNbO_3$ Using CASTEP Analysis 32
3.7.1 Band Structure 32
3.7.2 Density of State (DOS) 33
3.7.3 Optical Properties (Kramer-Kronig Relation) 34
3.8 Summary of Chapter 36

4 STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF UNSTRAINED $LiNbO_3$ 37
4.1 Introduction 37
4.2 Convergence Test for *k*-Point and Cut-Off Energy 37
4.3 Structural Properties of Unstrained $LiNbO_3$ 39
4.4 Electronic Properties of Unstrained $LiNbO_3$ 40
4.5 Optical Properties of Unstrained $LiNbO_3$ 44
4.6 Summary of Chapter 47

5 EFFECT OF STRAIN ON STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF $LiNbO_3$ 49
5.1 Introduction 49
5.2 Strain Effect on Structural Properties 49
5.3 Strain Effect on Electronic Properties 51
5.4 Strain Effect on Optical Properties 52
5.5 Summary of Chapter 55

6 CONCLUSION AND SUGGESTION FOR FUTURE WORK 56
6.1 Conclusion 56
6.2 Suggestion for Future Work 57

REFERENCES/BIBLIOGRAPHY 58

APPENDIX 68

BIODATA OF STUDENT 69

LIST OF PUBLICATIONS 70

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Structural parameters of $LiNbO_3$ from theoretical and experimental data	11
2.2	Band gap of $LiNbO_3$ from theoretical and experimental data	12
3.1	The lattice parameters and atomic positions of $LiNbO_3$ with R3*c* space group [90]	26
3.2	The convergence threshold parameters for the geometrical optimization calculation	28
4.1	The optimized lattice parameters and percentage deviation of $LiNbO_3$ crystal in this work compared to the experimental data and other theoretical work	40
4.2	The band gap of the $LiNbO_3$ calculated from various methods	42
4.3	Comparison of the dielectric constant, $\varepsilon_1(0)$ of $LiNbO_3$	46
5.1	Lattice parameter of the strained $LiNbO_3$	50

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	History of the ferroelectric [34]	8
2.2	Types of ferroelectric materials	9
2.3	LiNbO3 crystal structure [38]	10
2.4	Density of states (DOS) and partial density of states (PDOS) of $LiNbO_3$ [38]	13
2.5	Calculated real and imaginary part of the dielectric function of $LiNbO_3$ in its ferroelectric phase as a function of the photon energy (eV) given in the *xx* direction (left) and in the *zz* direction (right) [49]	14
2.6	Refractive index of $LiNbO_3$ [59]	15
2.7	The band gap as a function of uniaxial strain for Si wires at different size. Positive strain refers to uniaxial expansion while negative strain corresponds to its compression [74]	16
2.8	The energy band gap dependence on the various strains [75]	17
2.9	Real part of dielectric function of Ge: (a) strain change from 0% to +4% and (b) strain change from 0% to −4% [76]	18
2.10	Strain effect on (a) refractive index (b) reflectivity and (c) absorption constant α of CdSe nanowire [77]	18
3.1	Materials Studio Version 6.1	24
3.2	The flow of the simulation process in material modelling	25
3.3	Unit cell of $LiNbO_3$ in ball and stick view	27
3.4	The overview of calculation setting flow	29
3.5	Several properties that available in CASTEP calculation	30
3.6	Few properties that can be displayed using CASTEP analysis	31
3.7	Flow chart of computational method	31
3.8	Schematic diagram of behavior band structure between metal, semiconductor and insulator	33
4.1	Convergence test of $LiNbO_3$ for *k*-points	38
4.2	Convergence test of $LiNbO_3$ for cut-off energy	39
4.3	The total density of states and partial density of states of $LiNbO_3$ crystal. The Fermi energy is set at 0 eV	44
4.4	The dielectric functions real part for (100) direction of $LiNbO_3$	45

4.5	The dielectric functions imaginary part for (100) direction of $LiNbO_3$	45
4.6	The ordinary (n_o) and extraordinary (n_e) refractive index without and with scissor operator	47
5.1	The crystal structure of $LiNbO_3$ (red: oxygen; blue: niobium; purple: lithium). The red plane is AB-plane and blue plane is C-plane	50
5.2	The band gap of $LiNbO_3$ on the applied negative and positive strained for AB and C plane	51
5.3	Real part of dielectric function of $LiNbO_3$ under applied strain	52
5.4	Imaginary part of dielectric function of $LiNbO_3$ under applied strain	53
5.5	Calculated refractive index of $LiNbO_3$ crystal under applied strain	53
5.6	Calculated extinction coefficient of $LiNbO_3$ crystal under applied strain	54
5.7	Calculated absorption coefficient with applied strain of $LiNbO_3$ crystal	55

LIST OF ABBREVIATIONS

ADF	Amsterdam Density Functional
ATK	Atomistix Toolkit
CASTEP	Cambridge Serial Total Energy Package
CB	Conduction Band
CBM	Conduction Band Minimum
CT	Charge Transfer
DFT	Density Functional Theory
DOS	Density of States
GGA	Generalized Gradient Approximation
HK	Hohenberg-Kohn
KS	Kohn-Sham
LDA	Local Density Approximation
MS	Materials Studio
PDOS	Partial Density of States
ReRAM	Resistive Random-Access Memory
SCF	Self-Consistence Field
VASP	Vienna Ab initio Simulation Package
VB	Valence Band
VBM	Valence Band Maximum
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Research

In the past few years, scientist has found the special single crystals which are an important material for optical waveguides, mobile phones, piezoelectric sensors, optical modulators and various other linear and non-linear optical applications. Among these crystals, lithium niobate ($LiNbO_3$) is one of the mainly used due to its various applications in optics and quantum electronics [1]. $LiNbO_3$ crystal belongs to the class of the ferroelectric oxides. It has received much attention in recent years because of its unique combination of piezoelectric and electro-optic properties [2,3].

$LiNbO_3$ manifests itself into two phases depending on the temperature. Below the Curie temperature, T_c, $LiNbO_3$ behaves as a ferroelectric phase with space group R3*c*, meanwhile, beyond the T_c, it changes into the paraelectric phase (R*c*) [4]. Due to its high T_c (1210°C), only a few experimental data are available on the paraelectric phase while ferroelectric phase has been the subject of numerous experimental and theoretical studies [5–10].

In this work, the calculations based on the density functional theory (DFT) method were performed for structural properties (lattice parameters, volume, bond length) electronic properties (band structure, partial and total density of states) and optical properties (dielectric function, refractive index, absorption coefficient) of $LiNbO_3$ using Cambridge Serial Total Energy Package (CASTEP) computer code. The strain effect on the structural, electronic and optical properties of $LiNbO_3$ were investigated by applied the positive and negative strains on both AB and C planes of $LiNbO_3$ crystal. This was done by changing the lattice constant in the vertical and horizontal direction of the plane of $LiNbO_3$ where lattice constants along a-axis and c-axis are varied from -3% to +3%. This study is very important in obtaining desired properties and a high-quality film of $LiNbO_3$.

1.2 Problems Statement

In modern microelectronic and photonic products, the use of thin film is very important, and it can be produced using various techniques. Due to its crystalline structure, $LiNbO_3$ has advantages towards thin film growth processes [11]. However, during epitaxial growth, the lattice strain will occur, and this will affect the properties of the material such as band gap, carrier mobility, dielectric tensor and refractive index [12]. In the case of $LiNbO_3$ thin film, epitaxially grown on substrate material will cause the crystalline film to experience strongly compressive strain [13]. By now, the researches about the influence of strain on the properties of $LiNbO_3$ are limited. So, it is necessary to study the effect of strain on the structural, electronic and optical properties of $LiNbO_3$.

Most studies on $LiNbO_3$ focused on the crystal growth and lattice parameter [12,14,15], while many modifications were focused on doping [16,17], substitution [18] and vacancy induced [6,19]. Inspired by the literature of thin film effect, the properties of bulk $LiNbO_3$ can also be modified and tuned by the applied strain. For deposition of $LiNbO_3$ thin film, *c*-axis deposition orientation is preferable because, along this crystallographic direction, good piezoelectric properties with high electro-optic and nonlinear optical properties can be achieved [20–22]. Applying solid-phase crystallization of pre-deposited noncrystalline film, *a*-axis oriented $LiNbO_3$ deposition has been successfully grown by Akazawa [14]. However, no detail on its performance has been discussed. To date, there is still a lack of available literature discussing *a*-axis oriented $LiNbO_3$.

1.3 Objectives

Objectives of this research can be describe as follows:

1) To calculate the electronic band gap of $LiNbO_3$ crystal based on reverse scissor correction method.
2) To investigate the structural, electronic and optical properties of unstrained $LiNbO_3$ crystal structure.
3) To evaluate the effect of *a*-axis and *c*-axis oriented strain on the properties of $LiNbO_3$ crystal.

1.4 Significance of Research

Conventionally, the material studies always focused on mapping the synthesis-structure-property relations which required laborious effort and the results some time

not promising such as limitations of $LiNbO_3$. Hence, the computational approach is aiming to design the good performance of ferroelectric materials. Nowadays, the investigations of chemical and physical properties of multiferroic from the microscopic level using a first-principles study based on quantum mechanical DFT are crucial in scientific research. It is very important to have a high accuracy of the first-principles method that many experimental data and spectra can well reproduce. The application of the first-principles study not only limited to the fundamental knowledge but also can provide valuable information on the structural phase instability as well as one of the important tools in materials design. The main purpose of this work is to provide the theoretical approach for insight understanding and designing $LiNbO_3$ based on unstrained (strain-free) and strained structures. This insight of $LiNbO_3$ on the aspect of structural, electronic, and optical properties are useful for both fundamental science and technological applications.

1.5 Scope and Limitation of Research

In the present work, attention has been focused on the structural, electronic and optical properties of ferroelectric $LiNbO_3$. To ensure the accurate result, the validations on the functional (LDA and GGA) and convergence test toward *k*-point and cut-off energy were performed using CASTEP computer code. The properties such as lattice parameter, volume, band gap, density of states (DOS), dielectric function, refractive index and absorption coefficient for unstrained and strained $LiNbO_3$ were identified. To facilitate comparison with the experimental results, a scissor operator was applied to match the calculated optical gap with that determined via the experiment approach. For the strain effect on structural, electronic and optical

properties of $LiNbO_3$, the strain was changed from −3% to +3%. This strain tolerance is to ensure the structure remain on its original structural phase. Beyond this tolerance the phase change might occur.

1.6 Thesis Outline

This thesis is divided into six chapters. The first chapter provides an overview of research work including the background of research, problem statements, objectives, significance of research and thesis outline. Chapter two reviews the important information related to $LiNbO_3$ materials. Afterward, chapter three provides in detail the whole research methodology including the introduction of basic theoretical principles of the DFT method. In chapters four and five, the research finding was reported in detail, meticulously analyzed and discussed rigorously. Finally, chapter six presents the conclusions of research findings related to the objectives and discussed the impact of the finding from this research study for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, an overview of the ferroelectric materials is briefly presented. The types of ferroelectric materials are introduced to know the crystal group of the studied materials. The literature on the structural, electronic and optical properties of $LiNbO_3$ also highlighted with regards to the scope of the study. Lastly, the available literature on the effect on strain on band gaps, dielectric function, refractive index and absorption coefficient are also reported to understand the strain effect.

2.2 Ferroelectric Materials

Technological advancement nowadays is greatly relying on the development of advanced material. Technologies such as an ultra-sensitive actuator, sensor, ultrasonic transducer and piezoelectric will make the device become smaller, portable and high performance are the main requirements for many users [23,24]. These requirements inspired the material scientist and engineer to produce new materials that will push further the capability of existing technologies. These existing technologies are

fundamentally governed by several material properties and among them is ferroelectric.

Ferroelectric materials are characterized by having a polarization direction that can be switched in response to an external electric field, which generates many technical applications [25]. Ferroelectricity was first discovered by Valasek [26] in a complex compound which is called Rochelle salt (sodium potassium tartrate tetrahydrate) [27] and it was only material possessing the extraordinary property of reversible polarization. Afterward, which is around 1935, ferroelectricity was observed in potassium dihydrogen phosphate (KH_2PO_4). In the 1940s, the famous ferroelectric ceramics were discovered in polycrystalline barium titanate ($BaTiO_3$) [28]. Since then, there has been a continuous succession of new materials such as in $LiNbO_3$ and $LiTaO_3$ in 1949. This leads to a significant number of industrial and commercial applications for future technology developments. The history of the ferroelectric is summarized in Figure 2.1 [34] .

The types of ferroelectric materials according to their structure are corner-sharing oxygen octahedral, compounds containing hydrogen boned radicals, organic polymers and ceramic polymer composites as shown in Figure 2.2 [29]. The corner-sharing oxygen octahedral consist of the perovskite type compounds, lithium niobate and tantalite, bismuth oxide layer structured and tungsten bronze type compounds. Among these types, $LiNbO_3$ is one of the important categories. Therefore, $LiNbO_3$ has been used for both theoretical and practical purposes [30–33].

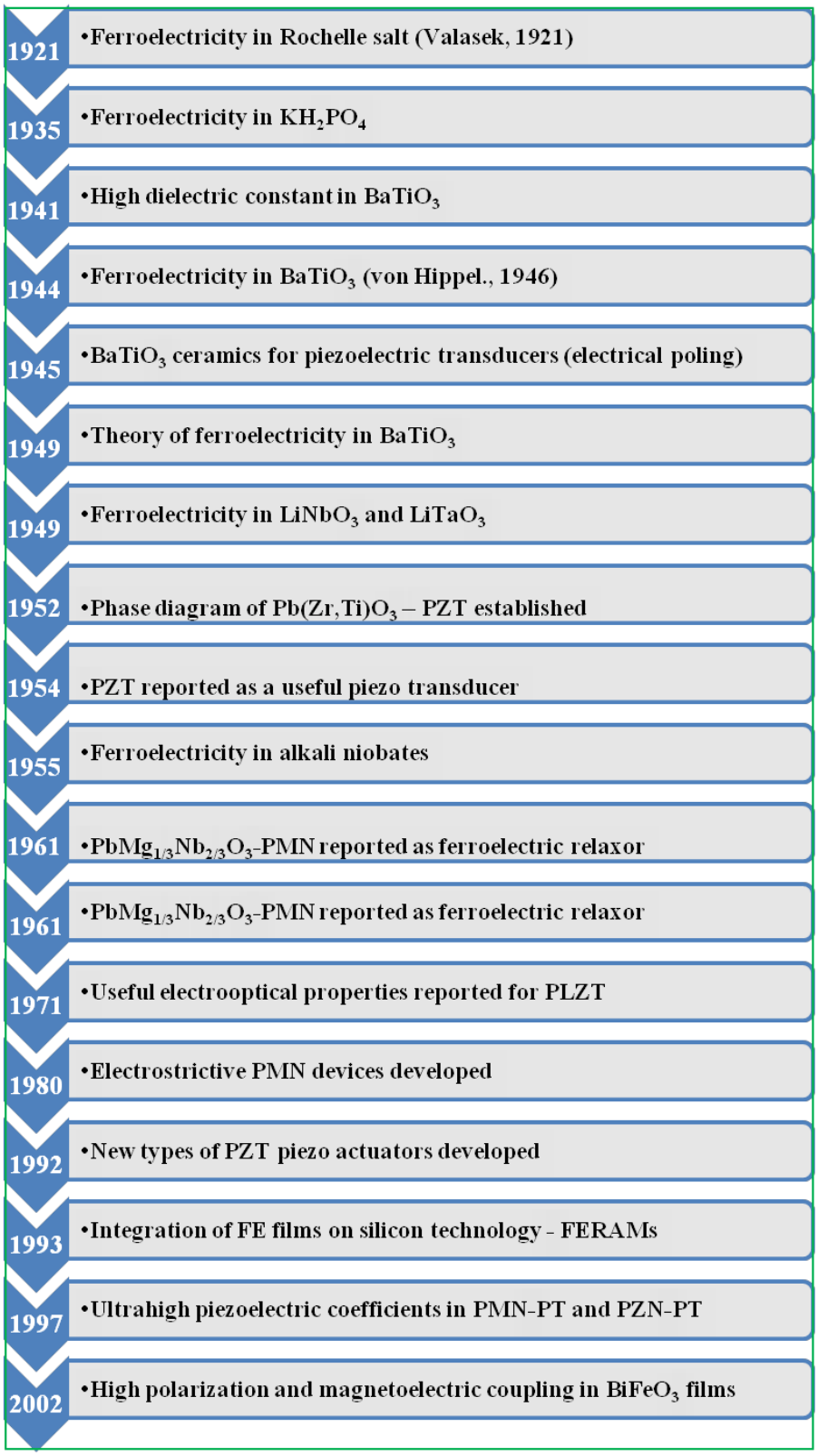

Figure 2.1 History of the ferroelectric [34]

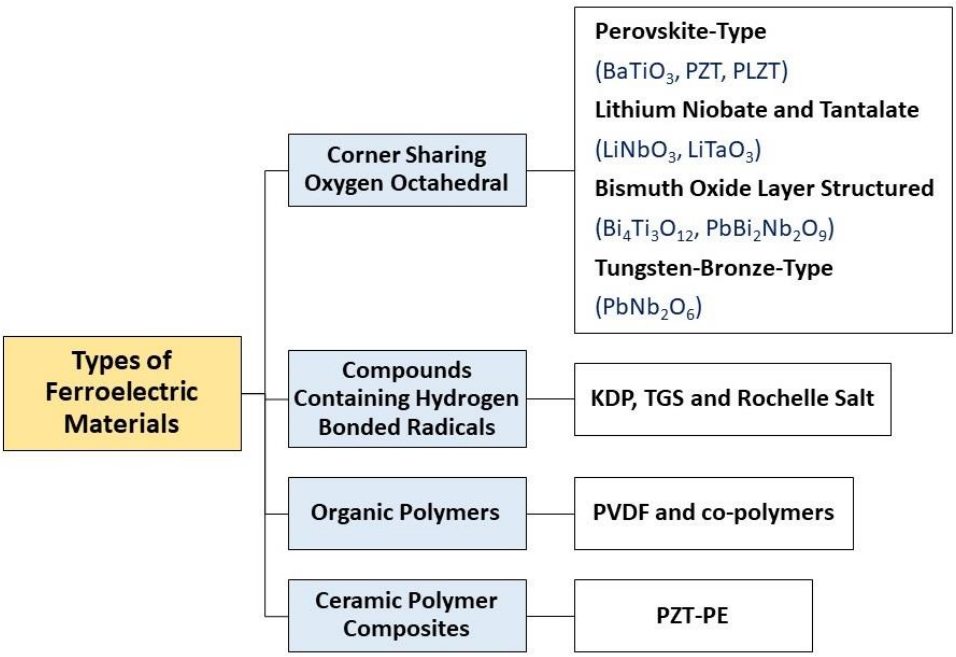

Figure 2.2 Types of ferroelectric materials [29]

2.3 Lithium Niobate

Lithium niobate ($LiNbO_3$) is one of the ferroelectric materials. It was first discovered to be ferroelectric in 1949 and it is human-made dielectric material which is not existed in nature [35]. In this single crystal, a multitude of different effects occurring such as ferroelectricity, pyroelectricity and optical nonlinearity [36]. This effect has been applied in various kind of application such as in modulators, storage devices, sensors, actuators, transducers, holographic memories, photorefractive devices, waveguide structures and frequency doublers [37].

The chemical formula for lithium niobate is $LiNbO_3$. $LiNbO_3$ crystal structure at the temperatures below its ferroelectric Curie temperature approximately 1210 $^{\circ}$C consists of planar sheets of oxygen (O) atoms in the distorted hexagonal close-packed configuration. The octahedral interstices formed in this structure are one third filled

by lithium (Li) atoms, one third filled by niobium (Nb) atoms and the other one third is vacant as illustrated in Figure 2.3 [35]. In the paraelectric phase above the Curie temperature, the Li atoms lie in O layer that is *c*/4 away from the Nb atom and the Nb atoms are centered between O layers. These positions make the paraelectric phase non-polar [35]. After that, as the temperature decreases from the Curie temperature, the elastic forces of the crystal become dominant and force the Li and Nb ions into new positions. The charge separation resulting from this movement of ions relative to the O octahedra makes $LiNbO_3$ exhibit spontaneous polarization at the temperatures below 1210 ˚C.

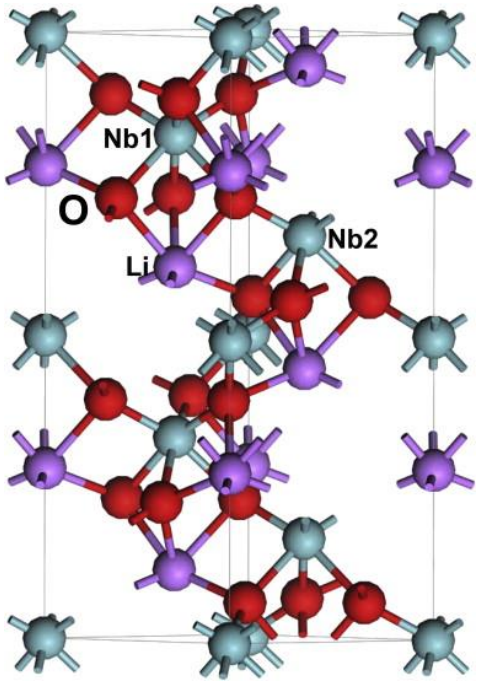

Figure 2.3 $LiNbO_3$ crystal structure [35]