TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iii
ABSTRACT (ENGLISH)	v
ABSTRACT (THAI)	vii
LIST OF TABLES	XV
LIST OF FIGURES	xvii
ABBREVIATIONS AND SYMBOLS	xxiii
CHAPTER 1 INTRODUCTION	1
1.1 Overview	1
1.2 Research objectives	2
1.3 Usefulness of the research	3
1.4 Research plan, methodology and scope	3
CHAPTER 2 THEORY AND LITERATURE REVIEW	4
2.1 Ferroelectric materials	4
2.1.1 Properties 2.1.1.1 Pyroelectric properties and spontaneous	5
polarization	5
2.1.1.2 Piezoelectric properties	7

	Page
2.1.2 Applications	7
2.1.3 Lithium niobate (LiNbO ₃)	9
2.2 Glass	12
2.2.1 Theory of glass	14
2.2.2 Raw materials for glass melting	17
2.2.3 Atomic hypothesis of glass formation	21
2.2.4 Nucleation and crystallization	22
2.2.5 Controlled crystallization	28
2.3 Glass-ceramics	29
2.3.1 History	29
2.3.2 Theory of glass-ceramics	30
2.3.3 Applications	31
2.4 Literature Review	32
2.4.1 Lithium-based glasses and glass-ceramics	33
2.4.1.1 Crystallization and glass formation in	
$50Li_2O \cdot 50Nb_2O_5$ and $25Li_2O \cdot 25Nb_2O_5 \cdot$	
50SiO ₂	33
2.4.1.2 Lithium niobate ferroelectric material obtained by glass crystallization	35
2.4.1.3 Evolution of ferroelectric LiNbO ₃ phase in a	
reactive glass matrix (LiBO ₂ · Nb ₂ O ₅)	37

х

2	2.4.2 Others ferroelectric-based glasses and glass-	
	ceramics	39
	2.4.2.1 Crystallization of Bi ₄ Ti ₃ O ₁₂ from glasses in	
	the system Bi ₂ O ₃ /TiO ₂ /B ₂ O ₃	39
	2.4.2.2 Crystallization of Bi ₃ TiNbO ₉ from glasses	
	in the system Bi ₂ O ₃ /TiO ₂ /Nb ₂ O ₅ /B ₂ O ₃ /SiO ₂	40
	2.4.2.3 Crystallization of ferroelectric bismuth	
	vanadate in $Bi_2O_3 \cdot V_2O_5 \cdot SrB_4O_7$ glasses	40
	2.4.2.4 $BiO_{1.5} \cdot BO_{1.5} \cdot GeO_2$ glass system and	
	crystallization of Bi ₄ Ge ₃ O ₁₂ phase	41
	2.4.2.5 Nanocrystallization of SrBi ₂ Nb ₂ O ₉ from	
	glasses in the system $Li_2B_4O_7 \cdot SrO \cdot Bi_2O_3 \cdot$	
	Nb ₂ O ₅	43
		4.5

CHAPTER 3 EXPERIMENTAL PROCEDURE	45
3.1 Samples preparation	45
3.1.1 LiNbO ₃ powder	45
3.1.2 Glass samples	47
3.1.3 Glass-ceramic samples	51
3.2 Glass and glass-ceramic samples characterization	52
3.2.1 Thermal analysis	52
3.2.2 Densification analysis	55

Page

3.2.3 Phase analysis	59
3.2.3.1 X-ray diffractrometry	59
3.2.3.2 Raman spectroscopy	60
3.2.4 Microstructural analysis	61
3.2.5 Measurement of optical properties	63
3.2.5.1 Transmittance (%)	63
3.2.5.2 Refractive index	66
3.2.6 Measurement of electrical properties	67
3.2.6.1 LiNbO ₃ · SiO ₂ glass and glass-ceramic	
system	67
3.2.6.2 LiNbO ₃ · SiO ₂ · Al ₂ O ₃ glass system	69

CHAPTER 4 RESULTS AND DISCUSSION (PART I):

LiNbO3 · SiO2 GLASS AND GLASS-CERAMIC	
SYSTEM	70
4.1 Appearance	71
4.1.1 Glass samples	71
4.1.2 Glass-ceramic samples	72
4.2 Thermal behavior determination	73
4.3 Densification investigation	77
4.4 Structural information	80
4.5 Microstructure observation	86

Page

	Page
4.5.1 Surface morphology of glass samples	86
4.5.2 Cross-sectional morphology of glass and glass-	
ceramic samples	91
4.6 Optical properties	98
4.6.1 Transmittance (%)	98
4.6.2 Refractive index	102
4.7 Electrical property	103
CHAPTER 5 RESULTS AND DISCUSSION (PART II):	
LiNbO3 · SiO2 · Al2O3 GLASS SYSTEM	109
5.1 Appearance	109
5.2 Thermal behavior determination	111
5.3 Structural information	112
5.3.1 X-ray diffractrometry	112
5.3.2 Raman spectroscopy	116
5.4 Microstructure observation	117
5.5 Electrical property	119
CHAPTER 6 CONCLUSIONS AND SUGGESTIONS FOR FURTURE	
All r _{work} hts reserv	e ₁₂₂
6.1 Conclusions	122
6.1.1 LiNbO ₃ \cdot SiO ₂ glass and glass-ceramic system	122

xiii

	1 age
$6.1.2 \text{ LiNbO}_3 \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ glass system	124
6.2 Suggestions for further work	124
REFERENCES	126
APPENDIX	137
VITA	153

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่ Copyright[©] by Chiang Mai University All rights reserved

xiv

LIST OF TABLES

Table		Page
2.1	Basic properties of lithium niobate.	10
2.2	Composition and characteristics of some common commercial	
	glasses.	13
2.3	Heat treatment conditions, visual appearance and phase compositions	
	of the sample L-4.	36
3.1	Specifications of the raw materials used for preparation LiNbO3	
	powder and glass samples.	46
3.2	Chemical compositions of the prepared glass samples.	50
3.3	The density of the fluid (distilled water) at various temperatures.	56
4.1	Typical DTA curves obtained for the powder of the glass samples	
	corresponding to the compositions.	75
4.2	Compositional variations of densities measured on the glass and	
	glass-ceramic samples at different heat treatment temperatures.	77
4.3	Compositional variations of densities measured on the glass and	
	glass-ceramic samples at different heating times.	79
4.4	Mean crystallite sizes (calculated by Scherrer equation) of glass-	
	ceramic samples at 600, 650, 700 and 975 °C for 1 h with 20, 25, 30	
	and 35 mol% SiO ₂ .	84

XV

Table		Page
4.5	Relative permittivity (ε_r) of glass and glass-ceramic samples at 600,	
	650, 700 and 975 °C for 1 h with 25 mol% SiO ₂ .	106
4.6	Relative permittivity (ε_r) of glass and glass-ceramic samples at 600,	
	650, 700 and 975 °C for 1 h with 30 mol% SiO ₂ .	107
4.7	Relative permittivity (ε_r) of glass and glass-ceramic samples at 600,	
	650, 700 and 975 °C for 1 h with 35 mol% SiO ₂ .	108
5.1	Peak intensity and mean crystallite sizes (calculated by Scherrer	
	equation) of quenched samples with 15, 25, 35, 45 and 55 mol%	
	SiO ₂ .	115
5.2	Relative permittivity (ε_r) of quenched samples with various	
	compositions.	121
6.1	Comparison relative permittivity value at room temperature and 1	
	kHz of glass samples in this research with others nearly research.	123

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่ Copyright[©] by Chiang Mai University All rights reserved

LIST OF FIGURES

Figure		Page
2.1	Polarization of (a) dielectric, (b) paraelectric and (c) ferroelectric.	6
2.2	Crystal structure of LiNbO ₃ showing the octahedral oxygen	
	coordination spheres of niobium.	11
2.3	Comparison of glass structure: (a) random amorphous structure and	
	(b) ordered crystalline structure.	12
2.4	Effect of temperature on the enthalpy of a glass forming melts.	16
2.5	Diagram of nucleation and crystallization.	23
2.6	Rates of homogeneous nucleation and crystal growth in a viscous	
	liquid.	27
2.7	Schematic diagram of idealized heat treatment; x: heating rate, y:	
	heat treatment temperature and z: dwell time.	28
2.8	Micrographs of surface morphologies of 50Li ₂ O · 50Nb ₂ O ₅ glass-	
	ceramics: (a) one-side quenching and (b) two-side quenching	33
29	XRD patterns of 50LicQ , 50Nh-Q- glass-ceramics: (a) one-side	
2.7	AND patterns of 50Li ₂ O · 50N0 ₂ O ₅ grass-cerannes. (a) one-side	34
Joyn	quenching and (b) two-side quenching.	54
2.10	XRD patterns of $25Li_2O \cdot 25Nb_2O_5 \cdot 50SiO_2$ glass-ceramics: (a) as-	
	quenching and (b) heat treatment at 800 °C for 30 min.	35
2.11	XRD patterns of the as-quenched ((a)-(b)) and the samples heat-	
	treated at 500 °C for 3 h ((c)-(f)).	38

xvii

Figure		Page
2.12	SEM records of the samples heat-treated at different temperatures:	
	(a) 475 °C, (b) 500 °C, (c) 600 °C and it shows voids/micro crack	
	formation and (d) 650 °C.	39
2.13	XRD patterns of the as-quenched samples ((a)-(c)) and the glass-	
	ceramic samples ((d)-(f)).	41
2.14	XRD pattern of the glass sample $(45BiO_{1.5} \cdot 40BO_{1.5} \cdot 15GeO_2)$.	42
2.15	SEM microphotographs of crystallized sample ($45BiO_{1.5} \cdot 40BO_{1.5} \cdot$	
	15GeO ₂): (a) prismatic crystals are $Bi_6B_{10}O_{24}$ and (b) pyramid-	
	shaped crystals are $Bi_4Ge_3O_{12}$.	42
2.16	XRD patterns of $40(Li_2B_4O_7) \cdot 60(SrO \cdot Bi_2O_3 \cdot Nb_2O_5)$ samples: (a)	
	as-quenched, heat-treated at (b) 450 °C, (c) 500 °C, (d) 550 °C and	
	(e) 625 °C and slow scan is shown in the inset.	44
3.1	Melting electric furnace.	48
3.2	Pouring melting glass onto a brass block.	48
3.3	Glass sample.	49
3.4	Annealing electric furnace.	49
3.5	Transparent glass sample.	51
3.6	Thermogravimetric analyzer.	53
3.7	Differential thermal analyzer.	54
3.8	Balance with density equipment.	58
3.9	Pycnometer.	58
3.10	X-ray diffractometer.	59

Figure		Page
3.11	Raman spectrometer.	61
3.12	Scanning electron microscope, equipped with EDX analyzer.	62
3.13	Transmission electron microscope.	62
3.14	UV-Vis-NIR spectrophotometer.	65
3.15	The absorbance spectrum of nickel, copper and nickel coin.	65
3.16	Impedance spectroscope (Kronach).	68
3.17	Roughly polished sample (left side) and after using gold-contacting	
	paste (right side): (a) top view and (b) side view.	68
3.18	Impedance spectroscope (Hewlett).	69
4.1	Glass samples with various compositions.	71
4.2	Transparency of glasses and glass-ceramics of four compositions.	72
4.3	DTA profiles of the glass samples with various compositions.	76
4.4	The glass transition temperature (T_g) and the temperature of the first	
	crystallization peak (T_{Cr1}) as a function of mol% SiO ₂ (error in the	
	temperatures \pm 10 K).	76
4.5	Densities of the glass and glass-ceramic samples at different heat	
	treatment temperatures.	78
4.6	Densities of the glass and glass-ceramic samples at different heating	
	times.	79
4.7	XRD patterns of glass samples with various compositions (red	
	arrow indicates cristobalite phase).	81
4.8	XRD patterns of glass and glass-ceramic samples with 20 mol%	
	SiO ₂ at different heat treatment temperatures.	82

Figure		Page
4.9	XRD patterns of glass and glass-ceramic samples with 25 mol%	
	SiO ₂ at different heat treatment temperatures.	83
4.10	XRD patterns of glass and glass-ceramic samples with 30 mol%	
	SiO ₂ at different heat treatment temperatures.	83
4.11	XRD patterns of glass and glass-ceramic samples with 35 mol%	
	SiO ₂ at different heat treatment temperatures.	84
4.12	XRD patterns of glass and glass-ceramic samples with 35 mol%	
	SiO ₂ at different heating times.	85
4.13	SEM and TEM micrographs of the glass sample with 20 mol $\%$ SiO ₂ .	87
4.14	SEM and TEM micrographs of the glass sample with 25 mol $\%$ SiO ₂ .	87
4.15	SEM and TEM micrographs of the glass sample with 30 mol $\%$ SiO ₂ .	88
4.16	SEM and TEM micrographs of the glass sample with 35 mol $\%$ SiO ₂ .	88
4.17	SEM and TEM micrographs of the glass sample with 40 mol $\%$ SiO ₂ .	89
4.18	SEM and TEM micrographs of the glass sample with 50 mol $\%$ SiO ₂ .	89
4.19	SEM micrographs (BSE detector) of heat-treated samples at 700 °C	
	for 1 h with 40, 45, 50 and 60 mol% SiO_2	90
4.20	SEM micrographs of the glass and glass-ceramic samples with 20	
	mol% SiO ₂ .	93
4.21	SEM micrographs of the glass and glass-ceramic samples with 25	
	mol% SiO ₂ .	94
4.22	SEM micrographs of the glass and glass-ceramic samples with 30	
	mol% SiO ₂ .	95

Figure		Page
4.23	SEM micrographs of the glass and glass-ceramic samples with 35	
	mol% SiO ₂ .	96
4.24	The optical transmission spectra and images of glass and glass-	
	ceramic samples with 25 mol% SiO_2 (minor scale = 1 mm).	99
4.25	The optical transmission spectra and images of glass and glass-	
	ceramic samples with 30 mol% SiO_2 (minor scale = 1 mm).	100
4.26	The optical transmission spectra and images of glass and glass-	
	ceramic samples with 35 mol% SiO_2 (minor scale = 1 mm).	101
4.27	Refractive index of glass samples.	102
4.28	Variation of relative permittivity $(\boldsymbol{\epsilon}_r)$ as a function of frequency with	
	25 mol% SiO ₂ .	104
4.29	Variation of relative permittivity (ε_r) as a function of frequency with	
	30 mol% SiO ₂ .	104
4.30	Variation of relative permittivity (ϵ_r) as a function of frequency with	
	35 mol% SiO ₂ .	105
4.31	Relative permittivity (ε_r) of glass and glass-ceramic samples with 25,	
	30 and 35 mol% SiO ₂ as heat-treated at 700 °C for 1 h.	105
5.1	Quenched samples with various compositions.	110
5.2	DTA profiles of the quenched samples with 15 mol% SiO ₂ .	111
5.3	XRD patterns of quenched samples with various compositions.	113
5.4	The relationship between 012 peak intensity and SiO ₂ content.	114
5.5	The relationship between the mean crystallite sizes and SiO ₂ content.	114

Figure		Page
5.6	Raman spectra of the quenched samples.	116
5.7	SEM micrographs of the quenched samples with various	
	compositions.	118
5.8	Relative permittivity of the quenched samples with various	
	compositions as a function of frequency.	120



ลิขสิทธิ์มหาวิทยาลัยเชียงใหม Copyright[©] by Chiang Mai University All rights reserved

xxii

xxiii

ABBREVIATIONS AND SYMBOLS

ASTM.	American society for testing materials
a.u.	arbitrary unit
BSE	back scattered electron
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EDX	energy dispersive X-ray spectrometry
eV	electron volt
F/m	farad per meter
FWHM	the full width at half maximum
g	gram
g/cm ³	gram per cubic centimeter
h	hour
HT	heat treatment
JCPDS	Joint Committee for Powder Diffraction Standards
К	Kelvin
kHz got	kilohertz Chiang Mai University
K/min	Kelvin per minute
kV	kilovolt
mA	milliampere
mg	milligram

MHz	megahertz
min	minute
mm	millimeter
mol%	percent molar
mW	milliwatt
NLO	nonlinear optical coefficients
nm	nanometer
OD OD	optical density
pm/V	picometer per volt
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
T _c	the Curie temperature
T _{Cr}	crystallization temperature
T _F	fictive temperature
Tg	glass transition temperature
T _m	melting temperature
T _n	nucleation temperature
UV-Vis-NIR	ultraviolet-visible-near infrared spectrophotometry
v	volt
wt%	percent weight
XRD	X-ray Diffraction
Å	angstrom

xxiv



ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่ Copyright[©] by Chiang Mai University All rights reserved