TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iii
ABSTRACT (ENGLISH)	v
ABSTRACT (THAI)	viii
LIST OF TABLES	xi
LIST OF ILLUSTRATIONS	xv
ABBREVIATIONS AND SYMBOLS	xxii
CHAPTER I: INTRODUCTION	
1.1 Introduction	1
1.2 Objectives	2
CHAPTER 2: RELATED THEORY AND LITERATURE SURVEYS	
2.1 Solid Solutions	3
2.1.1 Substitutional Solid Solutions	4
2.1.2 Interstitial Solid Solutions	7
2.1.3 Solid Solution of BaTiO ₃ Based	8
2.2 Theory of Sintering	14
2.2.1 Stages of Sintering	15
2.2.2 Solid-State Sintering	18
2.2.3 Liquid Phase Sintering	20
2.3 Dielectric Behavior of BaTiO ₃ Based Ceramics	23
2.4 Literature Surveys	24
2.4.1 Dielectric Properties of BaTiO ₃ Based Ceramics	24

2	.4.2 Effect of Low Sintering Aids on Dielectric Properties	30
	of BaTiO ₃ Based Ceramics	
СНАРТЕ	R 3: EXPERIMENTAL PROCEDURE	
3.1	Chemical Reagents	35
3.2	Synthesis Processing	35
3.3	Linear Shrinkage and Density Measurements	39
3.4	Characterisation	40
СНАРТЕ	R 4: RESULTS AND DISCUSSIONS OF CERAMIC IN THE	
	xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1- x)BaTiO ₃ SYSTEM	
4.1	Particle Size Analysis of Powders	44
4.2	Phase Identification by XRD	48
4.3	Lattice Parameter Estimation	59
4.4	Microstructure Evolution of	62
	xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1- x)BaTiO ₃ Ceramics	
4.5	Densification Measurement	66
4.6	Phase Distribution by Back-scattered Electron Imaging (BEI),	69
	X-ray Mapping and Energy Dispersive X-ray (EDX)	
4.7	Quantitative Phase Analysis	73
4.8	Dielectric Behaviour of xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1-x)BaTiO ₃ Ceramics	76
	by P1 Processing	
A 4.9	Dielectric Behaviour of xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1-x)BaTiO ₃ Ceramics	84
	by P2 Processing	

CHAPTER 5: RESULTS AND DISCUSSIONS OF $0.98BaTiO_3$ $0.02Ba(Mg_{1/3}Nb_{2/3})O_3\text{-WITH LOW MELTING POINT}$ ADDITIVES

PART	I	Ceramics in the $(100-x)0.02$ Ba $(Mg_{1/3}Nb_{2/3})O_3-0.98$ BaTi O_3 -	
		xBi ₂ O ₃ /Li ₂ CO ₃ System (S1 Ceramics)	
	5.1	Densification Measurement	91
	5.2	Phase Formation	94
	5.3	Lattice Parameters Estimation	99
	5.4	Microstructure Evolution	102
	5.5	Dielectric Properties	105
PART	II	Ceramics in the (100-x-y)0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃ -	
		xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO System (S2 Ceramics)	
	5.6	Densification Measurement	113
	5.7	Phase Formation	115
	5.8	Lattice Parameters Estimation	117
,	5.9	Microstructure Evolution	121
	5.10	Dielectric Properties	125
СНАР	TER	6: CONCLUSIONS	
	6.1	Conclusions	131
	6.2	Suggestions for Further Work	134
REFF	ERE	NCES I g h t s r e s e r v e	136
CIIDD	ICI)	I TIM VITAE	146

LIST OF TABLES

Tab	ole	Page
2.1	Common heterovalent substituents.	5
2.2	Ionic and crystal radius of some ions.	13
2.3	Stages of Sintering.	15
2.4	Sintering Mechanism.	18
3.1	Sample composition of additive-BMN in weight percent.	37
3.2	Sample compositions with sintering additives in weight percent.	38
4.1	Particle size of x Ba(Mg _{1/3} Nb _{2/3})O ₃ -(1- x)BaTiO ₃ by P1 and P2 processing.	45
4.2	Physical properties of sintered ceramics with varied x	68
	and sintering temperature.	
4.3	Average results of EPMA quantitative analysis of samples with varied x .	75
4.4	Dielectric properties of xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1-x)BaTiO ₃ by P1 processing.	83
4.5	Dielectric properties of xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1-x)BaTiO ₃ by P2 processing.	89
5.1	Phases identified by XRD in (100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	98
	-xBi ₂ O ₃ /Li ₂ CO ₃ samples.	
5.2	Dielectric properties of (100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	111
	$-xBi_2O_3/Li_2CO_3$ where $2 \le x \le 10$ (S1 Ceramics).	
5.3	Sample compositions of (100- <i>x-y</i>) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	112
	-xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO ceramics (S2 Ceramics).	
5.4	Phases identified by XRD in (100-x-y) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	120
	-xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO system.	

LIST OF ILLUSTRATIONS

Figu	ire	Page
2.1	Solid solution mechanisms involving substitution of heterovalent cations.	6
2.2	Schematic illustration of intrinsic point defects in a crystal of	8
	composition MX: (a) Anion and cation vacancy; (b) Perfect crystal;	
	(c) Cation vacancy and Interstitial cation.	
2.3	(a) Perovskite structure with B at origin and	9
	(b) with A at origin for BaTiO ₃ .	
2.4	Changes in dielectric constant of BaTiO ₃ as a function of temperature	10
	and crystallographic form.	
2.5	Development of the ceramic microstructure during sintering:	. 17
	(a) loose powder particles, (b) initial stage, (c) intermediate stage and	
	(d) final stage.	
2.6	Schematic diagrams of the classic liquid-phase sintering stages involving	21
	mixed powders which form a non reactive liquid on heating, allowing	
	subsequent particle rearrangement and densification by	
	solution-precipitation and solid skeleton sintering.	
2.7	Approximate ion displacements in the cubic-tetragonal distortion	24
	in BaTiO ₃ : (a) Cubic; (b) Shift of centers of positive and negative charges	2 0
	(c) Projection of tetragonal structure.	
3.1	Show the flow chart diagram of P1 and P2 processing.	42
3.2	Show the flow chart diagram of S1 and S2 processing.	43

Figu	ure	Page
4.1	(a) The particle size distribution of x Ba(Mg _{1/3} Nb _{2/3})O ₃ -(1- x)BaTiO ₃	46
	powder with as function of x prepared by P1 processing.	
	(b) The particle size distribution of xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1-x)BaTiO ₃	47
	powder with as function of x prepared by P2 processing.	
4.2	(a)Shows the XRD patterns of calcined powders	49
	of xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1-x)BaTiO ₃ which prepared by (a) P1 processing	
	(b) P2 processing; x indicating unidentified peak.	
	(b)Shows the XRD patterns of calcined powders	50
	of xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1-x)BaTiO ₃ which prepared by (a) P1 processing	
	(b) P2 processing; x indicating unidentified peak and * indicating as BMN	Γ.
4.3	X-ray diffractions of samples sintered at 1450°C from P1 processing	53
	showing; (a) phase formation with as a function of x and (b) second phase	
	formation; * indicating Ba ₆ Ti ₁₇ O ₄₀ .	
4.4	X-ray diffractions of 0.02 doped ceramic samples showing	55
٠	tetragonal peak splitting at high angles by (a) P1 and (b) P2 processing.	
4.5	X-ray diffractions of samples sintered at 1400°C from P2 processing	56
	showing; (a) phase formation with as a function of x and (b) second phase	
	formation; * indicating $Ba_6Ti_{17}O_{40}$, + : $Ba(Mg_{1/3}Nb_{2/3})O_3$ and x : $Ba_4MgTi_{17}O_{40}$	1 ₁ O ₂₇ .
4.6	X-ray diffraction patterns of ceramics showing phase formation	58
	with various sintering temperatures; (a) $x = 0.02$ added samples from P1	
	processing and (b) $x = 0.04$ added samples from P2 processing.	
	Second phase formation; * indicating Ba ₆ Ti ₁₇ O ₄₀ ,	
	+: $Ba(Mg_{1/3}Nb_{2/3})O_3$ and $x: Ba_4MgTi_{11}O_{27}$.	

Figu	ire	Page
4.7	Lattice parameters of x Ba(Mg _{1/3} Nb _{2/3})O ₃ - (1- x)BaTiO ₃	60
	as a function of x ; (a) P1 processing and (b) P2 processing.	
4.8	SEM micrograph of xBa(Mg _{1/3} Nb _{2/3})O ₃ - (1-x)BaTiO ₃ samples	61
	with (a) $x = 0.01$, (b) $x = 0.02$, (c) $x = 0.03$, (d) $x = 0.04$, (e) $x = 0.05$,	
	(f) $x = 0.06$ and (g) $x = 0.07$ sintered at 1450 °C for 2h by P1 processing.	
4.9	Shows the microstructure of $x = 0.02$ samples with prepared	62
	by P1 method, sintering at different temperature; 1300 °C, 1350 °C,	
	1400 °C and 1450 °C.	
4.10	SEM micrograph of xBa(Mg _{1/3} Nb _{2/3})O ₃ - (1-x)BaTiO ₃ samples	64
	with (a) $x = 0.01$, (b) $x = 0.02$, (c) $x = 0.03$, (d) $x = 0.04$, (e) $x = 0.05$,	
	(f) $x = 0.06$ and (g) $x = 0.07$ sintered at 1400 °C for 2h by P2 processing.	
4.11	Shows the microstructure of $x = 0.04$ samples with prepared	65
	by P2 processing, sintering at different temperature; 1350 °C,	
	1400 °C and 1450 °C.	
4.12	Density of sintered samples with P1 and P2 processing	66
	against different amount of x .	
4.13	Back scattering micrographs of $x = 0.02$, 0.04 and 0.07	71
	of additives ceramics prepared by (a) P1 and (b) P2 processing.	
4.14	Micrographs mapping of samples with $x = 0.07$ of additives prepared	72
	by P2 processing. SE = SEM micrograph,	
	BSE = Back scattering micrograph	
	and the bottom 4 pictures are the X-ray mapping	
	of Mg, Nb, Ti and Ba ions.	

Figu	re	Page
4.15	Temperature variation of dielectric constant ϵ_r of the	76
v	xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1- x)BaTiO ₃ ceramics, $x = 0$ -0.07	
	at 1 kHz with prepared by P1 processing.	
4.16	Maximum dielectric constant and transition temperature versus	77
	function of x with prepared by P1 processing.	
4.17	Log [($\mathcal{E}_{max}/\mathcal{E}$)-1] vs Log (T-Tm) for xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1-x)BaTiO ₃	80
	ceramics, $x = 0$ -0.05 with prepared by P1 processing.	
4.18	Temperature variation of tano of the x Ba(Mg _{1/3} Nb _{2/3})O ₃ -(1- x)BaTiO ₃	82
	ceramics, $x = 0$ -0.07 mole at 1kHz with prepared by P1 processing.	
4.19	Temperature variation of dielectric constant ε_r of the	85
	xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1- x)BaTiO ₃ ceramics, $x = 0$ -0.05 mole	
	at 1 kHz with prepared by P2 processing.	
4.20	Maximum dielectric constant and transition temperature	85
	versus function of x with prepared by P2 processing.	
4.21	Log [(ε_{max} / ε)-1] vs Log (T-Tm) for xBa(Mg _{1/3} Nb _{2/3})O ₃ -(1-x)BaTiO ₃	87
	ceramics, $x = 0$ -0.05 with prepared by P2 processing.	
4.22	Temperature variation of loss tangent tanδ of the xBa(Mg _{1/3} Nb _{2/3})O ₃	88
	- $(1-x)$ BaTiO ₃ ceramics, $x = 0$ -0.05 at 1kHz with prepared by P2 processing.	
5.1	Linear shrinkage (a) and density (b) of (100-x)0.02Ba(Mg _{1/3} Nb _{2/3})O ₃	93
	0.98BaTiO ₃ -xBi ₂ O ₃ /Li ₂ CO ₃ fired samples with as function of x against	
	sintering temperature.	

Fig	ure	Page
5.2	X-ray diffractions of (100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	94
	-xBi ₂ O ₃ /Li ₂ CO ₃ samples with as function of x sintered at 950 °C	
	and second phase formation; *indicating as second phases.	
5.3	Percentage of perovskite of (100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	97
	-xBi ₂ O ₃ /Li ₂ CO ₃ samples with as function of x against sintering temperatu	ire.
5.4	Tetragonality (c/a) of (100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	99
	-xBi ₂ O ₃ /Li ₂ CO ₃ samples with as function of x sintered at 950 °C.	
5.5	SEM micrograph of (100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	101
	-xBi ₂ O ₃ /Li ₂ CO ₃ samples with as function of x with sintered at 950 °C.	
5.6	Backscattered images of $x = 10$ specimen sintered at 950°C;	104
	(A) EDX from intergranular region labeled "spectrum1"; (B)	
	and (C) EDX from matrix grain labeled "spectrum2 and 3".	
5.7	Temperature variation of dielectric constant ε_r of the	105
	(100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃ -xBi ₂ O ₃ /Li ₂ CO ₃	
•	with as function of x at 1 kHz.	
5.8	Maximum dielectric constant and transition temperature of	106
	(100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃ -xBi ₂ O ₃ /Li ₂ CO ₃ samples	
	versus function of x .	
5.9	Temperature variation of dielectric loss tanδ of the	107
	(100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃ -xBi ₂ O ₃ /Li ₂ CO ₃	
	with as function of x at 1 kHz.	

Figu	ire	Page
5.10	$\text{Log}[(\varepsilon_{\text{max}}/\varepsilon)$ -1] vs $\text{Log}(\text{T-Tm})$ for (100-x) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃	110
	-0.98BaTiO ₃ - x Bi ₂ O ₃ /Li ₂ CO ₃ ceramics, $x = 2, 3, 4, 5, 6$ and 10	
	with prepared by S1 processing.	
5.11	Linear shrinkage (a) and Density (b) of (100-x-y) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃	114
	0.98BaTiO ₃ -xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO fired samples containing	
	different amounts of sintering aids against sintering temperature.	
5.12	X-ray diffractions of (100-x-y) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	115
	-xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO samples with as function of x,y sintered	
	at 950 °C and second phase formation; *indicating as second phases.	
5.13	Percentage of perovskite of (100-x-y) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	117
	-xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO system with as function of x,y against sintering	
	temperature.	
5.14	Lattice parameter (c/a) of 98.25[0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃]-	118
	1.32Bi ₂ O ₃ /Li ₂ CO ₃ -0.43PbO samples (Sample A)	
	against sintering temperature.	
5.15	Lattice parameter (a) of 92.99[0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃] -	119
	5.26Bi ₂ O ₃ /Li ₂ CO ₃ -1.75PbO samples (Sample C)	
	against sintering temperature.	
5.16	Microstructures of (100-x-y) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃	121
	-xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO ceramics sintered at 950 °C for 2 h.	
5.17	Backscattered images and EDX of Sample B sintered at 950°C	122
	at intergranular region (white area).	

Figure	
5.18 Micrographs mapping of Sample B; SE = SEM micrograph,	123
BSE = Backscattering micrograph and the bottom 3 pictures	
are the X-ray mapping of Bi, Ti and Ba.	
5.19 Dielectric constant at 1 kHz as a function of temperature for	125
$(100-x-y) 0.02$ Ba $(Mg_{1/3}Nb_{2/3})O_3-0.98$ Ba TiO_3-x Bi $_2O_3/Li_2CO_3-y$ Pb O_3	
ceramics sintered at 950°C and un-sintering aids.	
5.20 Maximum dielectric constant and transition temperature of	127
(100-x-y) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃ -xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO	306
samples sintered at 950°C against composition.	
5.21 Dielectric loss at 1 kHz as a function of temperature for	127
(100-x-y) 0.02Ba(Mg _{1/3} Nb _{2/3})O ₃ -0.98BaTiO ₃ -xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO	5 //
ceramics sintered at 950°C and un-sintering aids.) ///
5.22 SEM micrograph of Hexagonal phase in Sample B sintered at 950°	C. 128
5.23 $\text{Log}[(\mathcal{E}_{\text{max}}/\mathcal{E})-1] \text{ vs Log}(\text{T-Tm}) \text{ for } (100-x-y) \text{ 0.02Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}$	3 130
-0.98BaTiO ₃ -xBi ₂ O ₃ /Li ₂ CO ₃ -yPbO samples sintered at 950°C	
and un-sintering aids against composition.	

xxii

ABBREVIATIONS AND SYMBOLS

a Lattice Parameter a

BEI Backscattering Electron Image

BMN Ba(Mg_{1/3}Nb_{2/3})O₃

BT BaTiO₃

c Lattice Parameter c

EDX Energy Dispersive X-ray

EPMA Electron Probe Micro-analyzer

JCPDS Joint Committee for Powder Diffraction Standards

SEM Scanning Electron Microscopy

SEI Secondary Electron Image

tanδ Dielectric loss

ε_r Dielectric Constant

XRD X-ray Diffraction

 Nb_{τ}^{\bullet} a substitutional Nb ion on a Ti-site, net charge +1

 $V_{R_a}^{"}$ a barium ion vacancy, net charge -2

 $V_{Ti}^{m'}$ a Titanium ion vacancy, net charge -4

 $V_0^{\bullet\bullet}$ a oxygen ion vacancy, net charge +2

 $Mg_{T_i}^{"}$ a substitutional Mg ion on a Ti-site, net charge -2

 Li'_{Ba} a substitutional Li ion on a Ba-site, net charge -1

 Bi_{Ba}^{\bullet} a substitutional Bi ion on a Ba-site, net charge +1