

# TABLE OF CONTENTS

<b>ACKNOWLEDGEMENTS .....</b>	<b>viii</b>
<b>PREFACE.....</b>	<b>xii</b>
<b>TABLE OF CONTENTS .....</b>	<b>xviii</b>
<b>LIST OF TABLES .....</b>	<b>xxiii</b>
<b>LIST OF FIGURES .....</b>	<b>xxv</b>
<b>ABBREVIATIONS.....</b>	<b>xxxii</b>
<b>NOTATION.....</b>	<b>xxxiii</b>
<b>CHAPTER 1. Introduction and Literature Review.....</b>	<b>1</b>
1.1 Introduction .....	1
1.2 Piezoelectricity .....	4
1.3 Ferroelectricity .....	6
1.4 Landau Theory of Phase Transitions.....	7
1.5 Soft Phonon Modes .....	9
1.6 Differentiation of Ferroelectrics from Antiferroelectrics and Relaxor Ferroelectrics.....	10
1.7 Ferroelectric Perovskites .....	12
1.8 Morphotropic Phase Boundary .....	15
1.9 Phase Diagrams .....	16
1.10 Monoclinic Phases, Polarization Rotation and Origin of Enhanced Piezoelectric Responses .....	18
1.11 Toxicity of Pb.....	19
1.12 Recent Development in MPB-based Solid Solutions and Defect- Engineered Materials .....	20
1.13 Preliminary Studies on Ba(Cu <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> and its Solid Solution.....	24
1.14 Investigation of similar Solid Solutions with formulae (1-x) Ba(B' <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> - (x)PbTiO <sub>3</sub> ; B' = Mg, Zn, Yb, Lu, Sc .....	30
1.15 Objectives of the Thesis .....	31

**CHAPTER 2. Synthesis and Experimental Optimizations in (1-x)Ba(Cu<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-(x)PbTiO<sub>3</sub> Ceramics ..... 32**

2.1	Introduction .....	32
2.2	Brief Introduction of the Instruments used for Synthesis and Characterization of the (1-x)BCN-(x)PT Solid Solution .....	33
2.2.1	Ball Mill .....	33
2.2.2	Hydraulic Press .....	34
2.2.3	High-Temperature Furnace .....	35
2.2.4	X-Ray Diffractometer .....	36
2.2.5	Scanning Electron Microscope .....	37
2.2.6	X-ray photoelectron spectroscopy.....	38
2.2.7	Impedance analyzer.....	39
2.2.8	d <sub>33</sub> meter .....	40
2.2.9	P-E loop tracer.....	41
2.3	Synthesis of (1-x)Ba(Cu <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> -(x)PbTiO <sub>3</sub> Ceramics .....	42
2.3.1	Optimization of Calcination Conditions of (1-x)BCN-(x)PT Ceramics .....	43
2.3.2	Optimization of Sintering Conditions for Bulk Characterization of (1-x)BCN-(x)PT Ceramics .....	45
2.4	Instrumental Specification .....	45
2.5	Rietveld Structure Refinement Method for Crystal Structure Refinement...	46
2.5.1	Introduction .....	46
2.5.2	Details of the Rietveld Refinement .....	50

**CHAPTER 3. Room Temperature Crystal Structure of (1-x)Ba(Cu<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-(x)PbTiO<sub>3</sub> Ceramics ..... 51**

3.1	Introduction .....	51
3.2	Overview and Preliminary Picture of the phase evolution in (1-x)BCN-(x)PT Ceramics .....	52
3.3	Path Way for Finding Crystal Structure Solution .....	55
3.4	Notations and Nomenclature of Phases in (1-x)BCN-(x)PT Ceramics .....	57
3.5	Crystal Structure Progression and Illustration of Competing Crystal Structures for (1-x)BCN-(x)PT .....	58

3.5.1	Crystal Structure for the Composition Region $0.05 \leq x \leq 0.55$ .....	61
3.5.2	Crystal Structure for the Composition Region $0.59 \leq x \leq 0.60$ .....	63
3.5.3	Crystal Structure for the Composition Region $0.60 < x \leq 0.62$ .....	64
3.5.4	Crystal Structure for the Composition Region $0.62 < x \leq 0.65$ .....	66
3.5.5	Crystal Structure for the Composition Region $0.70 \leq x \leq 0.85$ .....	68
3.5.6	Crystal Structure for the Composition Region $0.85 < x < 1$ .....	71
3.6	Rietveld Refined Structural Parameters and Fit for the Entire Composition Range of $(1-x)\text{BCN}-(x)\text{PT}$ .....	75
3.7	Composition-Dependent Variation of Lattice Parameters and Phase Boundaries for $(1-x)\text{BCN}-(x)\text{PT}$ .....	86
3.8	Unit Cell Volume and Phase Separation in $(1-x)\text{BCN}-(x)\text{PT}$ Compositions	90
3.9	Conclusions .....	92

**CHAPTER 4. Temperature Dependent Crystal Structure Transitions and Phase Diagram of  $(1-x)\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3-(x)\text{PbTiO}_3$  Ceramics ..... 93**

4.1	Introduction .....	93
4.2	Temperature-Dependent Analysis of Relative Dielectric Permittivity of $(1-x)\text{BCN}-(x)\text{PT}$ Ceramics .....	95
4.3	Evolution of Crystal Structure as a function of Composition and Temperature for $(1-x)\text{BCN}-(x)\text{PT}$ Ceramics .....	97
4.3.1	Crystal Structures and Phase Transitions in the $x = 0.90$ Composition .....	99
4.3.2	Crystal Structures and Phase Transitions in the $x = 0.85$ Composition .....	104
4.3.3	Crystal Structures and Phase Transitions in the $x = 0.65$ and $0.70$ Compositions .....	110
4.3.4	Crystal Structures and Phase Transitions in the $x = 0.55, 0.60$ and $0.62$ Compositions .....	117
4.3.5	Phase Transitions in the Composition Regions $0 \leq x < 0.55$ and $0.90 < x < 1$ .....	125
4.4	Phase Diagram and Phase Transitions in $(1-x)\text{BCN}-(x)\text{PT}$ Ceramics .....	125
4.5	Phase Dynamics in $(1-x)\text{BCN}-(x)\text{PT}$ Ceramics .....	127
4.5.1	Phase Coexistence and Phase Separation in $(1-x)\text{BCN}-(x)\text{PT}$ Ceramics .....	127
4.5.2	Polar Cluster Formation and Random-Site Model .....	131
4.5.3	Diffraction Artefact and Nano-Domain Approach .....	133
4.6	Conclusion .....	136

**CHAPTER 5. Microstructural, Ferroelectric, Piezoelectric and Dielectric Properties of (1-x)Ba(Cu<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-(x)PbTiO<sub>3</sub> Ceramics ..... 136**

5.1	Introduction .....	136
5.2	Microstructural Studies of (1-x)BCN-(x)PT Ceramics.....	137
5.3	Compositional Analysis of (1-x)BCN-(x)PT from EDS and XPS.....	140
5.4	Dielectric Studies on (1-x)BCN-(x)PT Ceramics .....	145
5.5	Ferroelectric Studies on (1-x)BCN-(x)PT Ceramics.....	149
5.6	Composition Dependence of Piezoelectric Response in (1-x)BCN-(x)PT Ceramics.....	152
5.7	Summary and Conclusion .....	155

**CHAPTER 6. Effect of MnO<sub>2</sub> Additive on the Crystal Structure, Microstructure, Ferroelectric, Piezoelectric and Dielectric Properties of (0.38)Ba(Cu<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-(0.62)PbTiO<sub>3</sub> Ceramics..... 157**

6.1	Introduction .....	157
6.2	Crystal Structure Modifications in (0.38)BCN-(0.62)PT Ceramics by MnO <sub>2</sub> additive .....	159
6.3	Microstructural Studies .....	164
6.4	EDS Studies .....	167
6.5	Results of XPS Studies.....	168
6.6	Defect Chemistry for the MnO <sub>2</sub> added (0.38)BCN-(0.62)PT Ceramics.....	174
6.7	Temperature-Dependent Dielectric Studies on MnO <sub>2</sub> added (0.38)BCN-(0.62)PT Ceramics .....	177
6.8	Polarization Studies on MnO <sub>2</sub> added (0.38)BCN-(0.62)PT Ceramics.....	1833
6.9	Piezoelectric Response of Pure and MnO <sub>2</sub> added (0.38)BCN-(0.62)PT Ceramics.....	186
6.10	Conclusion.....	188

**CHAPTER 7. Summary and Future Scope..... 189**

7.1	Summary of the Thesis.....	189
7.1.1	Discovery of RT Crystal Structure for the Entire Composition Range of (1-x)Ba(Cu <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> -(x)PbTiO <sub>3</sub> Ceramics .....	189

7.1.2	Discovery of Crystal Structure of $(1-x)\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3-(x)\text{PbTiO}_3$ Ceramics from Cryogenic (15K) to High-Temperatures (1073K).....	190
7.1.3	Construction of New Phase Diagram.....	191
7.1.4	Physical Properties of the Solid Solution.....	192
7.1.5	Enhanced Responses of Ferroelectric, Dielectric and Piezoelectric Properties by the Addition of $\text{MnO}_2$ .....	193
7.2	Future Scope.....	193
<b>REFERENCES.....</b>		<b>195</b>
<b>LIST OF PUBLICATIONS .....</b>		<b>207</b>
<b>CONFERENCES AND WORKSHOPS ATTENDED .....</b>		<b>208</b>