

Table of contents

List of figures	xxi
List of tables	xxvii
Nomenclature	xxviii
1 Introduction and literature review	1
1.1 Motivation of thesis	1
1.2 Ferroelectricity	3
1.2.1 Definition, characteristics, and other related phenomena	4
1.3 Perovskite structure	8
1.3.1 Tolerance factor and structural stability	8
1.3.2 Theories to explain ferroelectricity in perovskites	10
1.3.3 Role of soft phonon modes in structural phase transformation of perovskites	12
1.3.4 Barium titanate: The first ferroelectric perovskite	13
1.4 Idea of phase coexistence in the enhancement of physical properties	16
1.4.1 Morphotropic and polymorphic phase boundary	17
1.5 Relaxor ferroelectrics	21
1.5.1 Definition and characteristics	21
1.5.2 Some models for relaxor ferroelectrics	25

1.6	Literature review on some BaTiO ₃ -based lead-free functional materials	29
1.6.1	(Ba,Ca)TiO ₃	29
1.6.2	Ba(Sn,Ti)O ₃	31
1.6.3	Ba(Zr,Ti)O ₃	35
1.6.4	(Ba,Ca)(Zr,Ti)O ₃	39
1.6.5	(Ba,Ca)(Sn,Ti)O ₃	41
1.7	Organisation of the thesis	43
2	Experimental procedure and characterization techniques	45
2.1	Sample synthesis	45
2.1.1	Solid-state reaction method	46
2.2	Characterization techniques	47
2.2.1	X-ray diffraction method	47
2.2.2	Dielectric measurement	51
2.2.3	Polarization vs. Electric field (PE) hysteresis loop measurements	53
2.2.4	Raman spectroscopic measurements	55
2.2.5	Microstructural measurement	57
3	Effect of calcium (Ca) dopant at ‘A’ site in tuning the ferroelectricity of average cubic ($Pm\bar{3}m$) phase in a perovskite (ABO₃)-based lead-free (Ba_{1-x}Ca_x)(Sn_{0.11}Zr_{0.05}Ti_{0.84})O₃ system	61
3.1	Introduction	61
3.2	Experimental procedure	64
3.3	Results and discussions	64
3.3.1	X-ray diffraction studies	64
3.3.2	Dielectric studies	67
3.3.3	Polarization vs. Electric field (PE) hysteresis loop analysis	72

3.3.4	Raman spectroscopic studies	74
3.4	Conclusion	79
4	Study of temperature-dependent crystallographic phase evolution in relaxor ferroelectric (Ba_{0.85}Ca_{0.15}) (Sn_{0.11}Zr_{0.05}Ti_{0.84})O₃ system	81
4.1	Introduction	81
4.2	Experimental procedure	82
4.3	Result and discussion	83
4.3.1	Temperature-dependent X-ray diffraction analysis	83
4.3.2	Temperature-dependent Raman spectroscopic studies	91
4.4	Conclusion	94
5	Role of ferroelectric soft phonon mode (Γ_4^-) in tuning the inter-ferroelectric phase boundary of lead-free (Ba_{0.92}Ca_{0.08}) (Zr_{0.05}Ti_{0.95-x}Sn_x)O₃; ($0 \leq x \leq 0.10$) system for enhanced ferroelectric polarization	95
5.1	Introduction	95
5.2	Experimental Procedure	97
5.3	Results and discussions	99
5.3.1	Microstructural analysis	99
5.3.2	Dielectric studies	102
5.3.3	Raman spectroscopic analysis	103
5.3.4	X-ray diffraction studies	107
5.3.5	Symmetry mode analysis	118
5.3.6	Polarization vs. Electric field (PE) hysteresis loop analysis	126
5.3.7	Temperature-dependent Raman spectroscopic studies	129
5.4	Conclusion	135

6	Relaxor ferroelectricity driven by microscopically off-centered atoms in the macroscopic cubic phase of lead-free $(\text{Ba}_{0.92}\text{Ca}_{0.08})(\text{Zr}_{0.05}\text{Ti}_{0.95-x}\text{Sn}_x)\text{O}_3$; ($0.125 \leq x \leq 0.25$) system	137
6.1	Introduction	137
6.2	Experimental methods	139
6.3	Results and discussions	140
6.3.1	X-ray diffraction studies	140
6.3.2	Dielectric studies	143
6.3.3	Raman spectroscopic studies	149
6.4	Conclusion	155
7	Summary and future work suggestions	157
7.1	Summary	157
7.2	Future work suggestions	160
	References	161