

Contents

1	A Preview of Concepts and Phenomena	1
2	Fundamentals of Ferroic Domain Structures	11
2.1	Structural Phase Transitions and Domain States: Basic Concepts and Classifications	11
2.1.1	Structural Changes at Phase Transitions: Ferroics	11
2.1.2	Ferroelectric Phase Transitions	16
2.1.3	Ferroelastics and Ferrobieflectrics	19
2.1.4	Higher Order Ferroics	28
2.1.5	Relation Between the Symmetries G and F: Order Parameter	32
2.1.6	Overview of Different Kinds of Phase Transitions: Species	35
2.1.7	Domain States	36
2.1.8	Ferroic Species	43
2.1.9	Ferroelectric Species	47
2.2	Coexisting Domain States	51
2.2.1	Twining Operations	52
2.2.2	Twin Laws for Nonferroelastic Domain Pairs	53
2.2.3	Domain Wall Orientation: Electrical Compatibility	58
2.2.4	Domain Wall Orientation: Mechanical Compatibility	62
2.2.5	Ferroelastic Domains in Physical Contact	66
2.2.6	Examples of Domain Wall Orientations: Nonferroelastic Walls	69
2.2.7	Examples of Domain Wall Orientations: Ferroelastic Walls	74
2.3	Thermodynamic Approach	81
2.3.1	Single-Component Order Parameter	81
2.3.2	Uniaxial Proper Ferroelectric (Nonferroelastic)	88
2.3.3	Uniaxial Proper Ferroelectric–Ferroelastic	91

2.3.4	Multiaxial Proper Ferroelectric–Improper Ferroelastic	92
2.3.5	Uniaxial Improper Ferroelastic–Ferroelectric	97
2.3.6	Limitation of Traditional Thermodynamic Approach: Pseudo-proper and Weak Ferroelectricity	100
3	Ferroic Materials	109
3.1	Sources of Information and Statistics	109
3.2	Table of Selected Ferroic Materials	110
4	Methods for Observation of Domains	121
4.1	Introductory Remarks	121
4.2	Surface Etching Techniques	122
4.3	Other Methods Based on Surface Relief	129
4.4	Surface Decoration Techniques	131
4.4.1	Colloidal Suspensions	132
4.4.2	Decoration by Sublimation and Vacuum Evaporation	134
4.4.3	Deposition in Liquids	136
4.4.4	Condensation of Vapor	136
4.4.5	Decoration by Liquid Crystal Layers	137
4.5	Scanning Force Microscopy-Based Techniques	142
4.5.1	Electrostatic Force Microscopy (EFM)	143
4.5.2	Scanning Surface Potential Microscopy (SSPM)	147
4.5.3	Contact Domain Imaging	149
4.5.4	Lateral Force Microscopy (LFM)	150
4.5.5	Domain Imaging via Surface Topography	151
4.5.6	Domain Imaging via Nonlinear Dielectric Response (SNDM)	153
4.5.7	Domain Imaging via Static Piezoresponse	155
4.5.8	Domain Imaging via Dynamic Piezoresponse (PFM)	158
4.6	Polarized Light Microscopy Based on Unperturbed Linear Optical Properties	161
4.6.1	Birefringence	161
4.6.2	Spatial Dispersion	169
4.6.3	Optical Activity	170
4.6.4	Optical Absorption and Observation in Reflected Light	172
4.7	Optical Methods Based on Higher Order Optical Properties	173
4.7.1	Perturbed Linear Optical Properties: Electro-optics and Elasto-optics	173
4.7.2	Nonlinear Optical Properties	176
4.7.3	Photorefractive Properties	179

4.8	Electron Microscopy	182
4.8.1	Scanning Electron Microscopy	182
4.8.2	Transmission Electron Microscopy	186
4.8.3	Electron Mirror Microscopy	193
4.9	Methods Based on Interactions with X-Rays	194
4.10	Pyroelectric Mapping	197
4.11	Scanning Optical Microscopy	200
4.12	Additional Methods and Concluding Remarks	203
5	Static Domain Patterns	207
5.1	Introductory Remarks and Scheme of the Chapter	207
5.2	Equilibrium 180° Domain Patterns in a Ferroelectric Plate: Theories	208
5.3	Domain Patterns Connected with Phase Boundaries	220
5.3.1	Perfect Matching	220
5.3.2	Matching on Average	222
5.4	Selected Observations of Domains in Crystalline Ferroic Samples	224
5.4.1	Uniaxial Ferroelectrics (Nonferroelastic) with the Second-Order Transition	225
5.4.2	Ferroelastics with a Small Number of Domain States	235
5.4.3	Perovskite Ferroics	253
5.4.4	R Cases	262
5.4.5	Quartz	265
5.4.6	Tweed Patterns	267
6	Domain Walls at Rest	271
6.1	Thickness and Structure of Domain Walls: Methods and Data	272
6.1.1	Direct Optical Observations	273
6.1.2	X-Ray and Neutron Scattering	278
6.1.3	X-Ray Topography	281
6.1.4	Raman Scattering	282
6.1.5	Electron Holography	283
6.1.6	Transmission Electron Microscopy	285
6.1.7	Surface Methods	288
6.1.8	Comments on Available Data	291
6.2	Macroscopic Theories of Domain Walls	291
6.2.1	Order Parameter Profile in Domain Walls	292
6.2.2	Effects of Strain Induced by the Order Parameter	300
6.2.3	Domain Walls in Selected Ferroics	305
6.2.4	Concluding Remarks	314
6.3	Microscopic Theories of Domain Walls	315

6.4	How Flat Is the Wall?	319
6.4.1	Mathematical Problem	321
6.4.2	Nonferroelectric/Nonferroelastic Walls	322
6.4.3	Walls in Ferroelectrics and Ferroelastics	325
6.4.4	Experimental Data on Roughening of Ferroic Domain Walls and Experimental Observations	328
7	Switching Properties: Basic Methods and Characteristics	331
7.1	Introduction	331
7.2	Ferroelectric Hysteresis Loop	332
7.3	TANDEL Effect	339
7.4	Pulse Switching	340
7.5	Ferroelastic Hysteresis Loops	344
7.6	More Involved Methods	349
8	Switching Phenomena and Small-Signal Response	351
8.1	Introduction and Overview of Switching Mechanisms	351
8.2	Basics of Domain State Reorientation	354
8.2.1	Driving Force for Processes of Domain State Reorientation	354
8.2.2	Pressure Acting on a Domain Wall	357
8.3	Single Domain Wall in Motion	360
8.3.1	Experimental Techniques Used to Measure Domain Wall Velocity	360
8.3.2	Motion of Ferroelectric Nonferroelastic Walls	364
8.3.3	Motion of Ferroelastic Walls in Ferroelectrics	382
8.4	Theories of Single Wall Motion	391
8.4.1	Two Regimes of Wall Motion	392
8.4.2	Wall Mobility in Activated Regime. Miller–Weinreich Theory	394
8.4.3	Wall Mobility in Activated Regime. Advanced Theories and Present Understanding of the Problem	397
8.4.4	Domain Wall Motion in Non-activated Regime	404
8.4.5	Domain Wall Motion Influenced by the Ferroelectric/Electrode Interface	410
8.4.6	Motion of Curved Domain Walls	415
8.5	Defect Pinning and Creep of Domain Walls	418
8.5.1	Non-thermally Assisted Regime, Weak and Strong Pinning	419
8.5.2	Finite Temperatures: Weak Pinning and Creep	422
8.5.3	Finite Temperatures: Strong-Pinning Regime	426
8.5.4	Weak and Strong Pinning with Flexible Defects	427
8.5.5	Experimental Evidence on Weak Pinning and Creep of Ferroelectric Domain Walls	428

8.6	Switching Process in Selected Materials	429
8.6.1	BaTiO_3	430
8.6.2	TGS and TGFB	438
8.6.3	LiTaO_3 and LiNbO_3	443
8.6.4	KDP and Isomorphous Crystals	446
8.7	Theory and Modeling of Switching	448
8.7.1	Introduction	448
8.7.2	Domain Nucleation	451
8.7.3	Domain Coalescence	457
8.7.4	Pulse Switching	459
8.7.5	Classical Polarization Hysteresis Loops	466
8.7.6	Rayleigh Loops	470
8.7.7	Piezoelectric Hysteresis Loops	475
8.7.8	Ferroelectric Breakdown	481
8.8	Extrinsic Contribution to Small-Signal Dielectric Response in Bulk Ferroelectrics	483
8.8.1	Introduction	483
8.8.2	Fully Immobile Domain Pattern	485
8.8.3	Contributions from Moving Domain Walls in Ideal Crystals	490
8.8.4	Quasistatic Bending Contribution from “Firmly” Pinned Domain Walls	498
8.8.5	Limited Motion of Free Domain Wall	501
8.8.6	Wall Motion in Random Potential and Dispersion of the Dielectric Response (Experimental Findings and Interpretation)	504
8.8.7	Domain Freezing	511
8.8.8	Dielectric Response Associated with Mobile Ferroelastic Domain Walls in a Clamped Multidomain Ferroelectric	515
9	Ferroelectric Thin Films	521
9.1	Introduction	521
9.2	Experimental Studies on the Static Domain Pattern in Thin Films	523
9.2.1	Domain Structure in (001) Thin Films of Tetragonal Ferroelectric Perovskites	523
9.2.2	Ferroelastic Domain Patterns in (001) Rhombohedral and (111) Tetragonal Thin Films of Ferroelectric Perovskites	536
9.2.3	Domain Structure in Other Systems	542
9.3	Domain Pattern and Elastic Effects	544
9.3.1	Strained State of Ferroelectric Film and Dislocation-Assisted Stress Release	544

9.3.2	Single-Domain State in a Strained Film	553
9.3.3	Domain Formation Driven by Elastic Effects: Basic Concepts.	560
9.3.4	Domain Formation Driven by Elastic Effects: Advanced Theoretical Results.	573
9.3.5	Domain Formation Driven by Elastic Effects: Theory vs. Experiment	589
9.4	Domain Pattern and Electrostatic Effects	599
9.4.1	Equilibrium Domain Pattern in Ferroelectric/ Dielectric Sandwich Structure.	599
9.4.2	Equilibrium Domain Pattern in Ferroelectric Films on Insulating Substrates	603
9.4.3	Limitations of Hard-Ferroelectric Approximation and Results Obtained Beyond This Approximation	604
9.5	Switching and Polarization Hysteresis	608
9.5.1	Pulse Switching	608
9.5.2	Ferroelectric Hysteresis Loops; Size Effects	613
9.5.3	Effects of Internal Bias and Imprint	627
9.6	Small-Signal Response	653
9.6.1	Intrinsic Contribution—Effect of Passive Layer	654
9.6.2	Intrinsic Contribution—Depletion Effect	662
9.6.3	Intrinsic Contribution—Strain Effect	664
9.6.4	Extrinsic Contribution—Mechanical Effects	667
9.6.5	Extrinsic Contribution—Electrostatic Effects	671
9.7	Polarization Fatigue in Thin Ferroelectric Films	677
9.7.1	How Can Imperfections Influence Polarization Switching in Ferroelectric Capacitor?	678
9.7.2	What Are These Imperfections and How Do They Affect the Switching Performance of Ferroelectric Capacitor?	686
9.7.3	Overall Picture of Polarization Fatigue in PZT Thin Films	688
9.8	Scanning Force Microscopy Study of Polarization Reversal	690
9.8.1	Top-Electrode-Free PFM	692
9.8.2	Through-Electrode PFM	700
9.9	Films of Proper Ferroelectric–Ferroelastics	704
Appendix A		713
Appendix B		715

Contents	xv
Appendix C	721
Appendix D	729
Appendix E	775
Appendix F	779
Transformation Laws for Tensors	779
Voight Notations for Tensors	779
Notation for Symmetry of Tensors	780
References	783
Index	813