

Contents

Preface — V

List of Contributing Authors — XIII

Thomas Lottermoser and Dennis Meier

1 A short history of multiferroics — 1

- 1.1 From ferroelectromagnets to multiferroics — 1
- 1.2 The second era of multiferroics — 4
- 1.3 What's next? — 7
- References — 8

Margarita D. Davydova, Konstantin A. Zvezdin, Alexander A. Mukhin and Anatoly K. Zvezdin

2 Spin dynamics, antiferrodistortion and magnetoelectric interaction in multiferroics. The case of BiFeO₃ — 13

- 2.1 Introduction — 13
- 2.2 The Lagrangian and Rayleigh dissipation function of a perovskite-like multiferroic — 16
- 2.3 The spin-wave spectrum — 20
- 2.4 Magneto-optical resonance — 22
- 2.5 Influence of the electric field on the magnon spectra — 24
- 2.6 Conclusion — 27
- Appendix — 27
- References — 32

Bernd Lorenz

3 Hexagonal manganites: Strong coupling of ferroelectricity and magnetic orders — 37

- 3.1 Introduction — 37
- 3.2 Preliminaries: structure, ferroelectricity, and magnetism — 38
- 3.3 The complex magnetic phase diagram and magnetoelectric effects in hexagonal HoMnO₃ — 43
 - 3.3.1 Dielectric properties, magnetic order, and thermodynamics of HoMnO₃ in the absence of magnetic fields — 44
 - 3.3.2 The magnetic phase diagram of HoMnO₃ — 47
 - 3.3.3 Low-temperature phases of HoMnO₃ — 51
 - 3.3.4 Evidence for strong spin–lattice coupling in HoMnO₃ through thermal expansion and magnetostriction measurements — 55
 - 3.3.5 Order of the Ho³⁺ magnetic moment and coupling to the Mn³⁺ spin structures in HoMnO₃ — 58

3.4	Hexagonal manganites RMnO_3 with nonmagnetic R-ions — 61
3.4.1	Multiferroic YMnO_3 — 61
3.4.2	Multiferroic properties of LuMnO_3 and ScMnO_3 — 65
3.4.3	InMnO_3 : Ferroelectric or not? — 67
3.5	Hexagonal manganites with magnetic rare earth ions — 70
3.5.1	Multiferroic properties and phase diagrams of ErMnO_3 , TmMnO_3 , and YbMnO_3 — 70
3.5.2	Metastable hexagonal DyMnO_3 — 77
3.6	Summary and outlook — 78
	References — 81

Takashi Kurumaji

4	Spiral spin structures and skyrmions in multiferroics — 89
4.1	Introduction — 89
4.2	Spin spiral orders and microscopic origins — 91
4.3	Origin of ferroelectricity in spiral spin systems — 94
4.4	Multiferroic triangular-lattice antiferromagnets — 96
4.4.1	Crystal structures — 96
4.4.2	Magnetism and ferroelectricity — 97
4.4.3	Generalized inverse DM mechanism in a triangular-lattice magnet — 100
4.4.4	d - p metal-ligand hybridization mechanism — 102
4.5	Skyrmion in noncentrosymmetric magnets — 104
4.6	Skyrmion-hosting multiferroics — 108
4.6.1	Cu_2OSeO_3 — 108
4.6.2	GaV_4X_8 ($\text{X} = \text{S}, \text{Se}$) — 110
4.6.3	VOSe_2O_5 — 112
4.7	Skyrmion in a centrosymmetric magnet — 113
4.7.1	Theoretical models — 114
4.7.2	Material design — 115
4.8	Summary and outlook — 117
	References — 117

Eric Bousquet and Andrés Cano

5	Non-collinear magnetism & multiferroicity: the perovskite case — 127
5.1	Introduction — 127
5.2	Preliminaries: a theory primer — 129
5.2.1	Classifying spin orders in magnetic perovskites — 129
5.2.2	Generalized Heisenberg model — 131
5.2.3	Basic mechanisms for multiferroicity — 134
5.3	Non-collinear orders in type-I multiferroic perovskites ($T_N \neq T_{FE}$) — 136

5.3.1	BiFeO₃ — 136
5.3.2	<i>Pbnm</i> perovskites — 137
5.4	Non-collinear orders in type-II multiferroic perovskites ($T_N = T_{FE}$) — 138
5.4.1	wFM and ferroelectricity — 138
5.4.2	Spiral order and ferroelectricity — 141
5.5	Conclusions — 147
	References — 148

Stephan Krohns and Peter Lunkenheimer

6	Ferroelectric polarization in multiferroics — 159
6.1	Introduction — 159
6.2	Signatures of ferroelectricity — 161
6.2.1	Signatures of ferroelectricity in dielectric spectroscopy — 161
6.2.2	Signatures of ferroelectricity in polarization measurements — 166
6.3	Ferroelectric signatures in various multiferroics — 168
6.3.1	Lone-pair multiferroicity in BiFeO₃ — 169
6.3.2	Geometrically driven improper ferroelectricity in <i>RMnO₃</i> — 171
6.3.3	Relaxor-ferroelectricity in magnetite — 176
6.3.4	Electric-dipole-driven magnetism in a charge-transfer salt — 179
6.3.5	Spin-driven improper ferroelectricity in DyMnO₃ — 181
6.3.6	Spin-driven improper ferroelectricity in the spin-1/2 chain cuprate system LiCuVO₄ — 182
6.4	Conclusions and outlook — 185
	References — 187

Marco Campanini, Rolf Erni and Marta D. Rossell

7	Probing local order in multiferroics by transmission electron microscopy — 193
7.1	Introduction — 194
7.2	S/TEM techniques for field mapping — 196
7.2.1	The spatial resolution of S/TEM phase-contrast techniques — 197
7.2.2	The electron beam sensitivity to electrostatic and magnetic fields — 198
7.2.3	Phase-contrast techniques in S/TEM — 201
7.2.4	Investigations of electric and magnetic ordering in multiferroic materials — 211
7.3	Electron nanodiffraction — 218
7.4	Strain mapping techniques — 220
7.4.1	Strain mapping from SEND techniques — 220
7.4.2	Strain mapping from Dark Field Electron Holography — 221
7.4.3	Strain mapping from high-resolution images — 222

- 7.5 Ferroelectric polarization mapping from high-resolution images — **226**
- 7.6 New possibilities of in situ measurements — **232**
- 7.6.1 Heating stages — **232**
- 7.6.2 Electrical stages — **234**
- 7.7 Summary — **238**
- References — **238**

David Szaller, Alexey Shuvaev, Alexander A. Mukhin, Artem M. Kuzmenko and Andrei Pimenov

- 8 Controlling of light with electromagnons — 249**
- 8.1 Introduction — **249**
- 8.2 Optical activity with electromagnons — **252**
- 8.2.1 Polarization rotation via magnetoelectric effect — **252**
- 8.2.2 Optical activity in samarium ferrobaborate — **256**
- 8.2.3 Optical activity in $\text{Ba}_2\text{CoGe}_2\text{O}_7$ — **259**
- 8.3 Directional anisotropy via the magnetoelectric coupling — **261**
- 8.3.1 One-way transparency by optical magnetoelectric effect in samarium ferrobaborate — **263**
- 8.3.2 One-way transparency by magneto-chiral dichroism in multiferroic $\text{Ba}_2\text{CoGe}_2\text{O}_7$ — **265**
- 8.4 Summary — **267**
- 8.5 Outlook — **267**
- References — **268**

Masahito Mochizuki

- 9 Dynamical magnetoelectric phenomena of skyrmions in multiferroics — 271**
- 9.1 Introduction — **272**
- 9.2 Magnetoelectric properties of Cu_2OSeO_3 — **276**
- 9.3 Spin model and phase diagram — **279**
- 9.4 Microwave nonreciprocal directional dichroism — **281**
- 9.5 Summary — **288**
- References — **289**

Julien Varignon, Nicholas C. Bristowe, Eric Bousquet and Philippe Ghosez

- 10 Magneto-electric multiferroics: designing new materials from first-principles calculations — 293**
- 10.1 Theoretical aspects — **295**
- 10.1.1 Computing ferroelectric properties — **296**
- 10.1.2 Modelling magnetic systems — **296**
- 10.1.3 Approximation of exchange and correlation effects — **297**

10.1.4	Computing the contribution to magneto-electric coupling —	298
10.1.5	Accessing finite temperature properties —	301
10.2	Strain engineering —	301
10.2.1	Inducing ferroelectricity in magnets —	301
10.2.2	Inducing magnetism in ferroelectrics —	304
10.2.3	Structural softness —	304
10.2.4	Phase competitions through spin-lattice coupling —	305
10.3	Oxide interfaces —	307
10.4	Lattice mode couplings —	309
10.4.1	The concept of lattice improper ferroelectricity —	309
10.4.2	Hybrid improper ferroelectricity —	311
10.4.3	Embedding ferroelectricity and octahedra rotation in a single phonon mode —	313
10.4.4	Triggered-like ferroelectrics —	314
10.5	Spin, charge and orbital induce ferroelectricity —	315
10.5.1	Magnetically induced ferroelectricity —	315
10.5.2	Charge-order induced ferroelectricity —	318
10.5.3	Orbital-order induced ferroelectricity —	318
10.6	Interfacial systems for efficient magneto-electrics —	319
10.6.1	Charge carrier mediated magneto-electric effect —	319
10.6.2	Ferroelectric control of magnetic order —	321
10.6.3	Ferroelectric control of magnetic easy axis, orbital occupancies and Curie temperature —	322
10.7	Conclusions —	322
	References —	323

Donald M. Evans, Vincent Garcia, Dennis Meier and Manuel Bibes

11	Domains and domain walls in multiferroics —	335
11.1	Domain structures in (multi-)ferroics —	335
11.1.1	Introduction to ferroic domains and domain walls —	335
11.1.2	Visualization of domains —	340
11.2	Domain walls in multiferroics —	344
11.2.1	Domain wall types —	345
11.2.2	Conduction in domain walls —	347
11.2.3	Magnetism at domain walls —	352
11.3	Manipulating domains and domain walls —	354
11.3.1	Electric control of antiferromagnetic domains —	354
11.3.2	Magnetic control of domain wall charge states in improper ferroelectrics —	357
11.3.3	Tailoring topological states in multiferroics —	359
11.4	Conclusions —	361
	References —	361

Elzbieta Gradauskaite, Peter Meisenheimer, Marvin Müller, John Heron and Morgan Trassin

12 Multiferroic heterostructures for spintronics — 371

12.1 Introduction — **371**

12.1.1 Magnetoelectric multiferroic heterostructures — **372**

12.1.2 Energy-efficient spintronics — **374**

12.2 Acting on magnetic order with electric fields in multiferroic heterostructures — **374**

12.2.1 Magnetostriction and electric field control of magnetic anisotropy — **375**

12.2.2 Electric field control of exchange bias — **377**

12.2.3 Electric-field-induced magnetization reversal — **378**

12.3 Ferroic domains and domain imprint in thin-film heterostructures — **380**

12.3.1 Ferroelectric domain engineering — **380**

12.3.2 Domain imprint — **383**

12.3.3 Domain wall engineering — **386**

12.4 Devices based on magnetoelectric thin films — **388**

12.4.1 Magnetoelectric/multiferroic memory — **388**

12.4.2 Magnetoelectric/multiferroic Logic — **392**

12.4.3 Neuromorphic devices — **392**

12.4.4 Hybrid magnetoelectric-spin-orbit torque heterostructures — **394**

12.5 Future perspectives and concluding remarks — **395**

12.5.1 Magnetoelectric switching dynamics — **395**

12.5.2 Towards all-optical magnetoelectric switching — **397**

12.6 Conclusion — **399**

References — **400**

Index — 413