

Contents

Foreword *ix*

Part I Theories and Fundamentals 1

- 1 Electron Transport Model in Nano Bulk Thermoelectrics 3**
 - 1.1 History of Conducting Oxides 3
 - 1.2 Structural Characteristics of Oxides 8
 - 1.3 Band Structure of Conventional Oxides 11
 - 1.4 Electrical Properties 11
 - 1.5 Model for Thermoelectric Oxides 15
 - 1.6 Effect of Interface on Electron Transport 17
 - References 22

- 2 Controlling the Thermal Conductivity of Bulk Nanomaterials 25**
 - 2.1 Bonding and Lattice Vibration 25
 - 2.2 Lattice Distortions in Determining Thermal Properties 25
 - 2.2.1 Point Defects and Dislocations 25
 - 2.2.2 Peierls Distortion 27
 - 2.2.3 Octahedral Distortion in Manganite Perovskites 28
 - 2.3 Callaway Model and the Minimum Thermal Properties 30
 - 2.4 Temperature Relationship in Thermal Properties 32
 - 2.5 Model for Lattice Thermal Conductivity 36
 - 2.5.1 Kinetic Theory 36
 - 2.5.2 Boltzmann Equation 36
 - 2.5.3 Phonon–Phonon Collisions 38
 - 2.6 Interfacial Thermal Conductivity 40
 - 2.7 Model for Nano Bulk Materials 43
 - 2.8 Minimum Value for Oxides 48
 - References 49

Part II Materials 53**3 Nonoxide Materials 55**

- 3.1 Bi₂Te₃-Based Materials 55
- 3.2 Skutterudite-Based Materials 59
- 3.3 Si-Ge Alloys 62
- 3.4 Other Alloy Materials 66
- References 71

4 Binary Oxides 77

- 4.1 Introduction for ZnO 77
- 4.2 Property of ZnO 77
 - 4.2.1 Structure 77
 - 4.2.2 Lattice Parameters 77
 - 4.2.3 Electronic Band Structure 77
 - 4.2.4 Mechanical Properties 79
 - 4.2.5 Thermal Expansion Coefficients 79
 - 4.2.6 Thermal Conductivity 80
 - 4.2.7 Specific Heat 80
 - 4.2.8 Electrical Properties of Undoped ZnO 81
- 4.3 Doping for ZnO-Based Thermoelectric Materials 81
- 4.4 ZnO Nanostructures 84
- 4.5 Introduction for In₂O₃ 87
- 4.6 Property of In₂O₃ 88
 - 4.6.1 Structure 88
 - 4.6.2 Electronic Band Structure 89
 - 4.6.3 Thermal Properties and Electrical Properties 89
- 4.7 Doping for In₂O₃-Based Thermoelectric Materials 90
- 4.8 In₂O₃ Nanostructures 94
- 4.9 TiO₂ and Others 98
- References 101

5 Perovskite-Type Oxides 105

- 5.1 Introduction for Perovskite-Type Oxides 105
- 5.2 Crystal Structure and Electronic Structure of Perovskite-Type Oxides 106
 - 5.2.1 Crystal Structure 106
 - 5.2.2 Electronic Structure 107
- 5.3 A- and B-Sites Doping for Perovskite-Type Oxides 108
 - 5.3.1 SrTiO₃ 108
 - 5.3.2 CaMnO₃ 109
 - 5.3.3 LaCoO₃ 111
- 5.4 Double Perovskites 112
 - 5.4.1 Structure of Double Perovskites 112
 - 5.4.2 Thermoelectric Properties of A'A''B₂O_{5+δ} 113
 - 5.4.3 Thermoelectric Properties of A₂B'B''O₆ 113
 - 5.4.4 Doping Modulation 115

5.4.5	Composite Ceramics	118
5.5	Nanostructure Property Relationships in Perovskite-Type Oxides	120
	References	124
6	Oxide Cobaltites	133
6.1	Introduction	133
6.2	Na_xCoO_2	133
6.3	$\text{Ca}_3\text{Co}_4\text{O}_9$	138
6.3.1	Single Dopants of $\text{Ca}_3\text{Co}_4\text{O}_9$	139
6.3.2	Dual Dopants of $\text{Ca}_3\text{Co}_4\text{O}_9$	144
6.3.3	Texture for $\text{Ca}_3\text{Co}_4\text{O}_9$	147
6.3.4	Nanocomposites for $\text{Ca}_3\text{Co}_4\text{O}_9$	147
6.4	New Concepts for Oxide Cobaltites	150
	References	151
7	Promising Complex Oxides for High Performance	155
7.1	Crystal Structure–Property Relationships	155
7.2	History of Complex Superconductors	156
7.3	Ternary Oxyselenides	158
7.3.1	Donor Doping on $[\text{Bi}_2\text{O}_2]^{2+}$ Layers	158
7.3.2	Donor Doping on $[\text{Se}]^{2-}$ Layers	160
7.3.3	The Solid Solution of $\text{Bi}_2\text{O}_2\text{Se}$ and $\text{Bi}_2\text{O}_2\text{Te}$	160
7.4	Quaternary Oxyselenides	164
7.4.1	Thermoelectric Properties	166
7.4.2	Band Gap Tuning	168
7.4.3	Texturing	168
7.4.4	Modulation Doping	169
7.4.5	Nanocompositing	171
7.5	Complexity Through Disorder in the Unit Cell	173
7.6	Complex Unit Cells	174
	References	176
8	New Thermoelectric Materials and Nanocomposites	179
8.1	Nanocomposite Design	180
8.1.1	Energy-filtering Design	180
8.1.2	All-Scale Hierarchical Architectures	181
8.1.3	Quantum Nanostructured Bulk Materials	183
8.2	Organic Thermoelectric Materials	183
8.2.1	p-Type Organic Thermoelectric Materials	184
8.2.2	PEDOT	184
8.2.3	PANI	187
8.2.3.1	The Molecular Structure of PANI	188
8.2.3.2	Conductive Mechanism of PANI	188
8.2.3.3	Synthesis of PANI	188
8.2.3.4	Electrochemical Method	189
8.2.4	Doping of PANI	189
8.2.5	Tuning the Work Function of Polyaniline	190

- 8.2.6 n-Type Thermoelectric Materials 192
- 8.3 Organic/Inorganic Thermoelectric Nanocomposites 192
 - 8.3.1 0D Nanoparticles/Polymer 192
 - 8.3.2 1D Nanowires or Nanotubes/Polymer 193
 - 8.3.3 2D Nanosheets/Polymer 197
- References 201

Part III Devices and Application 207

- 9 Oxide Materials Preparation 209**
 - 9.1 Synthesis Method of Nanopowder 209
 - 9.1.1 Solid-State Reaction 209
 - 9.1.2 Solution Preparation 210
 - 9.1.2.1 Sol–Gel Method 211
 - 9.1.2.2 Precipitation and Coprecipitation Method 211
 - 9.1.2.3 Hydrothermal Method 213
 - 9.1.3 Gas-Phase Reaction 214
 - 9.2 Advanced Bulk Technology 214
 - 9.2.1 Spark Plasma Sintering 215
 - 9.2.2 Hot-Press Sintering 215
 - 9.2.3 Microwave Sintering 217
 - 9.2.4 Two-Step Sintering 218
 - 9.2.5 Phase-Transformation Sintering 219
 - 9.3 Sintering Conditions on the Properties of Bulk 219
 - 9.3.1 Effect of Sintering Temperature 219
 - 9.3.2 Effect of Sintering Atmosphere 220
 - 9.3.3 Effect of the Addition for Sintering 220
 - References 221
- 10 Modeling and Optimizing of Thermoelectric Devices 229**
 - 10.1 Introduction to Thermoelectric Devices 229
 - 10.2 The Theoretical Analysis 230
 - 10.3 The Model Design 232
 - 10.4 The Interfaces in Thermoelectric Modules 236
 - 10.5 The Simulation and the Optimization 238
 - 10.6 The Measurement Theories and Systems 241
 - 10.7 All-oxide Thermoelectric Device 242
 - References 245
- 11 Photovoltaic Application of Thermoelectric Materials and Devices 247**
 - 11.1 Introduction 247
 - 11.2 Photovoltaic–Thermoelectric Integration Devices 248
 - 11.3 Photoelectric–Thermoelectric Composite Materials 253
 - References 260

Index 263