

Contents

Foreword	xiii
Preface	xv
1. Introduction	1
1.1 General	1
1.2 Preparative Methods	3
1.3 Scope of the Book	5
2. Combustible Solid Precursors to Nanocrystalline Oxide Materials	9
2.1 Introduction	9
2.2 Combustible Metal Hydrazine and Metal Hydrazine Carboxylate Complexes	11
Part I: Metal Hydrazine Carboxylates: Precursors to Simple Metal Oxides	14
2.3 Preparation of Metal Formate, Acetate, Oxalate, and Hydrazine Carboxylates	14
2.3.1 Thermal Analysis and Combustion of Metal Hydrazine Carboxylates	16
Part II: Single Source Precursors to Mixed Metal Oxides	26
2.4 Mixed Metal Oxides	26
2.4.1 Mixed Metal Acetate and Oxalate Hydrazinates: Precursors to Cobaltites	27

2.4.2	Mixed Metal Oxalate Hydrazinates: Precursors to Spinel Ferrites	27
2.4.3	Mixed Metal Oxalate Hydrates: Precursors to Metal Titanates	30
2.5	Mixed Metal Hydrazinium Hydrazine Carboxylates	30
2.5.1	Mixed Metal Hydrazinium Hydrazine Carboxylates: Precursors to Nano-Cobaltites and Ferrites	30
2.5.2	Mixed Metal Hydrazinium Hydrazine Carboxylates: Precursors to Mixed Ferrites	35
2.5.3	Mixed Metal Hydrazinium Hydrazine Carboxylates: Precursors to Manganites	37
2.6	Concluding Remarks	38
3.	Solution Combustion Synthesis of Oxide Materials	42
3.1	Introduction	42
3.2	Solution Combustion Synthesis (SCS)	43
3.2.1	Synthesis of Alumina	45
3.2.2	Mechanism of Aluminum Nitrate — Urea Combustion Reaction	46
3.2.3	Thermodynamic Calculation	48
3.3	Role of Fuels	49
3.4	A Recipe for the Synthesis of Various Classes of Oxides	53
3.4.1	Recipe for Nanomaterials	56
3.5	Salient Features of Solution Combustion Method	58
4.	Alumina and Related Oxide Materials	61
4.1	Introduction	61
4.2	Alumina and Related Oxide Materials	62
4.3	α -Alumina	65
4.4	Metal Aluminates (MA_2O_4)	68
4.5	Rare Earth Orthoaluminates ($LnAlO_3$)	73
4.6	Garnets	74
4.7	Aluminum Borate	78
4.8	Tialite (β - Al_2TiO_5)	80
4.9	Aluminum Phosphate	83

4.10	Alumina Composites	84
4.10.1	Al ₂ O ₃ · SiO ₂ System: Mullite	85
4.10.2	Al ₂ O ₃ · SiO ₂ System: Cordierite	87
4.10.3	Al ₂ O ₃ · Si ₃ N ₄ System: SiAlON	91
4.11	Alumina Nanocomposites	93
4.11.1	Nanocatalysts, Dispersion of Nano-metals (Ag, Au, Pd, and Pt) in Al ₂ O ₃	94
4.12	Nanopigments	99
4.12.1	Cobalt-Based Blue Alumina and Aluminates	99
4.12.2	Chromium-Doped Pink Alumina (Cr ³⁺ /Al ₂ O ₃): Ruby	104
4.12.3	Chromium-Doped Aluminates and Orthoaluminates (Cr ³⁺ /MAl ₂ O ₄ (M = Mg & Zn)) and LaAlO ₃)	105
4.13	Nanophosphors	106
4.13.1	Phosphor Materials (Luminescence in Aluminum Oxide Hosts)	108
4.14	Concluding Remarks	114
5.	Nano-Ceria and Metal-Ion-Substituted Ceria	117
5.1	Introduction	117
5.2	Synthesis and Properties of Nano-Ceria	119
5.3	Synthesis of Metal-Ion-Substituted Ceria	121
5.4	Characterization of Metal-Ion-Substituted Ceria	124
5.5	Oxygen Storage Materials	132
5.6	Metal-Ion-Substituted Ceria as Nanocatalysts	137
5.6.1	Ce _{1-x} Pd _x O _{2-δ} as a Three-Way Catalyst	141
5.6.2	Ce _{1-x} Pt _x O _{2-δ}	146
5.6.3	Ce _{1-x} Rh _x O _{2-δ}	147
5.6.4	Bimetal Ionic Catalysts (Ce _{1-x} Pt _{x/2} Rh _{x/2} O _{2-δ})	149
5.7	Concluding Remarks	151
6.	Nanocrystalline Fe₂O₃ and Ferrites	154
6.1	Magnetic Materials	154
6.2	γ-Fe ₂ O ₃	156
6.3	Spinel Ferrites (MFe ₂ O ₄)	158
6.4	Mixed Metal Ferrites	161

6.4.1	Li–Zn Ferrites	161
6.4.2	Mg–Zn Ferrites	165
6.4.3	Ni–Zn Ferrites	167
6.5	Rare Earth Orthoferrites	170
6.6	Garnets ($\text{Ln}_3\text{Fe}_5\text{O}_{12}$)	171
6.7	Barium and Strontium Hexaferrites	174
6.8	Concluding Remarks	177
7.	Nano-Titania and Titanates	179
7.1	Introduction	179
7.2	Nano-TiO ₂ (Anatase)	182
7.2.1	Synthesis and Properties of Nano-TiO ₂ (Anatase) . . .	183
7.3	Photocatalytic Properties of Nano-TiO ₂	189
7.4	Metal-Ion-Substituted TiO ₂	197
7.4.1	Synthesis and Photocatalytic Properties of Ti _{1-x} M _x O _{2-δ} (M = Ag, Ce, Cu, Fe, V, W, and Zr) . .	197
7.4.2	Synthesis and Properties of Ti _{1-x} Pd _x O _{2-δ}	199
7.4.3	Catalytic Properties of Ti _{1-x} Pd _x O _{2-δ}	200
7.5	Titanates for Nuclear Waste Immobilization	203
7.5.1	Sintering and Microstructure Studies	208
7.6	Concluding Remarks	209
8.	Zirconia and Related Oxide Materials	212
8.1	Introduction	212
8.2	Zirconia	213
8.2.1	Preparation and Properties of ZrO ₂	215
8.3	Stabilized Zirconia	220
8.3.1	Magnesia-Stabilized Zirconia	221
8.3.2	Calcia-Stabilized Zirconia	223
8.3.3	Yttria-Stabilized Zirconia (YSZ)	225
8.3.4	Nickel in Yttria-Stabilized Zirconia (Ni-YSZ)	227
8.4	Nano-Zirconia Pigments	232
8.5	ZrO ₂ –Al ₂ O ₃ System: ZTA	235
8.6	ZrO ₂ –CeO ₂ System	238
8.7	ZrO ₂ –TiO ₂ System (ZrTiO ₄ and Zr ₅ Ti ₇ O ₂₄)	242

8.8	ZrO ₂ -Ln ₂ O ₃ System: Pyrochlores	245
8.9	NASICONs	247
8.9.1	MZr ₂ P ₃ O ₁₂ (M = Na, K, 1/2 Ca, and 1/4 Zr) and NbZrP ₃ O ₁₂	247
8.9.2	NASICON (Na Superionic Conductor) Materials (Na _{1+x} Zr ₂ P _{3-x} Si _x O ₁₂)	251
8.10	Concluding Remarks	254
9.	Perovskite Oxide Materials	256
9.1	Introduction	256
9.2	Dielectric Materials	256
9.2.1	MTiO ₃ , MZrO ₃ (M = Ca, Sr, and Ba)	258
9.2.2	Lead-Based Dielectric Materials (PbTiO ₃ , PbZrO ₃ , PZT, and PLZT)	259
9.3	Relaxor Materials (PFN, PMN, PNN, and PZN)	265
9.4	Microwave Resonator Materials	270
9.5	Preparation and Properties of LnMO ₃ (M = Cr, Mn, Fe, Co, and Ni)	276
9.6	Preparation and Properties of La _{1-x} Sr _x MO ₃ (M = Mn and Fe)	281
9.7	Concluding Remarks	289
10.	Nanocrystalline Oxide Materials for Special Applications	292
10.1	Synthesis and Properties of Simple Oxides	292
10.2	Metal Silicates	295
10.3	Ceramic Pigments	298
10.3.1	Borate Pigments	299
10.3.2	Metal Chromite Pigments	302
10.3.3	Silicate Pigments	305
10.3.4	Ceria-Based Pigment — Ce _{1-x} Pr _x O _{2-δ}	308
10.4	Eu ³⁺ -Ion-Doped Red Phosphors	313
10.5	Metal Vanadates	318
10.6	Rare Earth Metal Oxides (La ₂ MO ₄)	320
10.7	Concluding Remarks	327

Appendix A	330
A.1 Oxidizers (Metal Nitrates)	330
A.1.1 Preparation of Titanyl Nitrate ($\text{TiO}(\text{NO}_3)_2$)	330
A.2 Fuels	331
A.2.1 Carbohydrazide (CH), $\text{CH}_6\text{N}_4\text{O}$	331
A.2.2 Oxalyl Dihydrazide (ODH), $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$	332
A.2.3 Tetraformal Trisazine (TFTA), $\text{C}_4\text{H}_{16}\text{N}_6\text{O}_2$	332
A.2.4 N, N'-Diformyl Hydrazine (DFH), $\text{C}_2\text{H}_4\text{N}_2\text{O}_2$	332
A.2.5 Maleic Hydrazide (MH), $\text{C}_4\text{H}_4\text{N}_2\text{O}_2$	333
A.2.6 Malonic Acid Dihydrazide (MDH), $\text{C}_3\text{H}_8\text{N}_4\text{O}_2$	333
A.2.7 3-Methyl Pyrazole 5-One (3MP5O), $\text{C}_4\text{H}_6\text{N}_2\text{O}$	333
A.3 Useful Suggestions	334
Index	337