

Contents

List of Contributors xix
Preface to the Second Edition xxi

1. Introduction 1

R.-R. Xu

- 1.1 Chemistry of Inorganic Synthesis 1
- 1.2 Major Scientific Issues in Modern Inorganic Synthetic Chemistry 2
 - 1.2.1 Development of New Synthetic Reactions, Synthetic Routes, Technologies, and Associated Basic Scientific Studies 2
 - 1.2.2 Sustainability in Modern Inorganic Synthetic Chemistry 3
 - 1.2.3 Basic Research on Synthetic and Preparative Routes Under Specific and Extreme Conditions 4
 - 1.2.4 Biomimetism as Tools in Bioinspiration in Modern Inorganic Synthesis 4
 - 1.2.5 Rational Synthesis and Molecular Engineering of Inorganics With Specific Structure and Function 5
- References 6

2. High Temperature Synthesis 9

R.-R. Xu, Q. Su

- 2.1 Attainment of High Temperature: Laboratory Furnaces and Related Techniques 9
 - 2.1.1 Resistance Furnaces 9
 - 2.1.2 Crystal Grower Equipment 9
 - 2.1.3 Arc Melting Furnace 10
 - 2.1.4 Spark Plasma Sintering 10

2.2 Types of High-Temperature Synthetic Reactions and Routes 11

- 2.2.1 High-Temperature Solid–Solid State Synthetic Reactions 11
- 2.2.2 High-Temperature Solid–Gas State Synthetic Reactions 11

2.3 High-Temperature Solid-State Reaction 11

- 2.3.1 Mechanism and Characters of Solid-State Reaction 12
- 2.3.2 Some Aspects of Synthesis Via Solid-State Reaction 13

2.4 Preparation of Rare Earth Containing Materials 14

- 2.4.1 Oxides and Complex Oxides 14
- 2.4.2 Halides 16
- 2.4.3 Chalcogenides 16
- 2.4.4 Pnictides and Oxypnictides 18

2.5 Sol–Gel Process and Precursors in High Temperature Solid Synthesis 19

- 2.5.1 The Chemistry of Sol–Gel Synthesis 20
- 2.5.2 The Precursors in High Temperature Solid-State Synthesis 22

2.6 Self-Propagating High-Temperature Synthesis 23

- 2.6.1 General Aspects 23
- 2.6.2 Chemical Classes of Self-Propagating High-Temperature Synthesis Reactions 24
- 2.6.3 Self-Propagating High-Temperature Synthesis Process and Its Characterization 27
- 2.6.4 Activation of Self-Propagating High-Temperature Synthesis Processes 27

- 2.7 **High-Temperature Preparation of Metal Vapors and Active Molecules for Use in Cryosynthesis** 29
- 2.7.1 Techniques of Metal Vapor Preparation 30
- 2.7.2 Attainment of High-Temperature Species 30
- 2.8 **High Temperature Electrolysis in Molten Salt System** 33
- 2.8.1 Basic of Molten Salt Electrolysis 33
- 2.8.2 Electrochemical Series of Molten Salts 33
- 2.8.3 Anode Effect 34
- 2.8.4 Examples of Molten Salt Electrolysis: Rare Earth Metal Preparation 35
- 2.8.5 Other Applications of Synthesis by Molten Salt Electrolysis 38
- References 39
- 3. Synthesis and Purification at Low Temperatures** 45
- W.-Q. Pang, Y. Xu
- 3.1 **Attainment and Measurement of Low and Ultralow Temperatures** 45
- 3.1.1 Attainment 45
- 3.1.2 Thermometry 46
- 3.2 **Vacuum Technique and Its Applications in Inorganic Synthesis** 46
- 3.2.1 Vacuum Attainment 47
- 3.2.2 Vacuum Measurement Principles and Typical Measurement Ranges 48
- 3.2.3 Common Vacuum Systems in Laboratory 48
- 3.3 **Purification and Separation of Inorganics at Low Temperatures** 52
- 3.3.1 Low-Temperature Fractional Condensation 52
- 3.3.2 Low-Temperature Fractional Distillation 53
- 3.3.3 Low-Temperature Selective Adsorption 55
- 3.3.4 Low-Temperature Chemical Separation 56
- 3.4 **Synthesis of Volatile Inorganic Compounds at Low Temperatures** 57
- 3.4.1 Synthesis of High-Purity AsF_5 57
- 3.4.2 Syntheses of $\text{R}_3\text{SiCo}(\text{CO})_4$ -Type Compounds 57
- 3.5 **Formation of Noble Gas Compounds Under Cryogenic Conditions** 58
- 3.5.1 Synthesis of $\text{Xe}[\text{PtF}_6]$ 59
- 3.5.2 Photochemical Synthesis of KrF_2 59
- 3.5.3 Synthesis of HXY Molecules by Matrix Photogeneration 60
- 3.5.4 Synthesis of Stable Argon Compounds 61
- 3.6 **Freeze-Drying Synthesis** 61
- 3.6.1 Locational Homogeneity of Reactants 62
- 3.6.2 Avoidance of Particle Agglomeration and Coarsening for Improved Size Uniformity 62
- 3.6.3 Aligned Two- and Three-Dimensional Structures by Ice-Templating 63
- 3.7 **Inorganic Synthesis in Liquid Ammonia** 63
- 3.7.1 Reactions of Metals With Liquid Ammonia 63
- 3.7.2 Reactions of Nonmetals With Liquid Ammonia 64
- 3.7.3 Ammonolysis of Inorganic Compounds in Liquid Ammonia 64
- 3.7.4 Substitution Reactions in Liquid Ammonia 64
- 3.7.5 Synthesis of $\text{MgCl}_2 \cdot 6\text{NH}_3$ in Liquid Ammonia 64
- 3.8 **Cryosynthesis of Unusual Inorganic Compounds** 67
- 3.8.1 Classification of Cryo-Synthetic Reactions 67
- 3.8.2 Basic Apparatus for Synthetic Reactions 70
- References 70
- 4. Hydrothermal and Solvothermal Syntheses** 73
- S.-H. Feng, G.-H. Li
- 4.1 **Foundation of Hydrothermal and Solvothermal Syntheses** 73
- 4.1.1 Features of Hydrothermal Synthetic Reactions 73
- 4.1.2 Classification of Hydrothermal Reactions 74
- 4.1.3 Property of Reaction Medium 75

- 4.2 **Functional Materials From Hydrothermal and Solvothermal Systems** 76
- 4.2.1 Single Crystals 78
- 4.2.2 Zeolites and Related Materials 79
- 4.2.3 Organic–Inorganic Hybrid Materials 82
- 4.2.4 Ionic and Electronic Conductors 84
- 4.2.5 Nanomaterials 86
- 4.3 **Hydrothermal Biochemistry** 87
- 4.3.1 Warm Pond: Hydrothermal Seafloor 87
- 4.3.2 Evolutionary Tree and Time Evidence 87
- 4.3.3 Chemical Ladder: Synthesis and Evolution 88
- 4.3.4 Expectation 89
- 4.4 **Supercritical Water: A Novel Reaction System** 89
- 4.4.1 Properties of Supercritical Water 90
- 4.4.2 Chemical Applications of Supercritical Water 91
- 4.4.3 Technological Applications of Supercritical Water 93
- 4.5 **Techniques and Methods** 93
- 4.5.1 Reaction Containers 93
- 4.5.2 Reaction Control Systems 96
- 4.5.3 General Experimental Procedure 96
- 4.5.4 In Situ Characterization Techniques 96
- 4.6 **Ionothermal Synthesis** 97
- References 100
5. **High Pressure Synthesis and Preparation of Inorganic Materials** 105
- X.-Y. Liu
- 5.1 **Experimental Methods of Inorganic Synthesis Under High Pressure** 106
- 5.1.1 High-Pressure Apparatus 106
- 5.1.2 The Choice of Pressure-Transmitting Media 109
- 5.1.3 Pressure Calibration 110
- 5.1.4 Generation of High-Temperature 112
- 5.1.5 Summary 114
- 5.2 **Effects of High Pressure on Basic States of Matter** 115
- 5.2.1 Gas Under High Pressure 115
- 5.2.2 Solids Under High Pressure 116
- 5.2.3 Water Under High Pressure 118
- 5.3 **Effects of High Pressure on Inorganic Chemical Reactions** 119
- 5.3.1 Influence of Pressure on Thermodynamics and Dynamics of Inorganic Reaction 119
- 5.3.2 The Impact of Pressure on Inorganic Reaction 120
- 5.4 **Effects of High Pressure on Crystal and Electronic Structures of Inorganic Compounds** 121
- 5.4.1 Changes in Crystal Structure at High Pressure 121
- 5.4.2 Electronic Structure Changes Under High Pressures 124
- 5.5 **Major Roles of High-Pressure Method in Inorganic Synthesis** 126
- 5.5.1 High Pressure Could Prevent the Decomposition of Thermally Unstable Starting Reagents 127
- 5.5.2 High-Pressure Can Improve the Densification Effect and Consequently Help the Preparation of Compact Structures 127
- 5.5.3 High-Pressure Can Decrease Reaction Temperature and Shorten Reaction Time 128
- 5.5.4 High Pressure Can Stabilize the Highest Oxidation States of Transition Metals Through the Development of High Oxygen or Fluorine Pressures 128
- 5.5.5 High Pressure Can Hinder the Disproportionation of Intermediate Oxidation States 129
- 5.5.6 High Pressure Aids in Synthesis of Light Element Compounds That Have Special Physical Properties 129
- 5.5.7 Preparation of Important Amorphous and Quasi-Crystalline Materials Using High-Pressure Methods 129
- 5.5.8 Conclusion 129

- 5.6 **Some Important Inorganic Compounds Synthesized Under High Pressure** 130
- 5.6.1 Synthesis of Diamond Under High Pressure 130
- 5.6.2 Synthesis of Cubic Boron Nitride (c-BN) Under High Pressure 131
- 5.6.3 High Pressure Synthesis of C_3N_4 132
- 5.6.4 The Synthesis of Superconductors Under High Pressure 133
- 5.6.5 The High Pressure Synthesis and Properties of the Compounds Containing Special Oxidation State Transition Metals 134
- 5.6.6 Summary 135
- References 135
- 6. Inorganic Photochemical Synthesis** 143
- X.-S. Liu*
- 6.1 Introduction 143
- 6.2 The Basic Concepts 143
- 6.2.1 Photon Energy 144
- 6.2.2 Light Absorption 144
- 6.2.3 Quantum Yield 145
- 6.3 Experimental Techniques 145
- 6.3.1 Light Sources 145
- 6.3.2 Reactors 145
- 6.3.3 Photon Actinometer 145
- 6.4 Photochemical Synthesis of Organometallic Complexes 146
- 6.4.1 Photosubstitution 146
- 6.4.2 Photoisomerization 149
- 6.4.3 Photosensitized Metal–Metal Bond Cleavage Reaction 150
- 6.4.4 Photoinduced Electron Transfer and Redox Reactions 150
- 6.5 Photochemical Synthesis of Inorganic Compounds 151
- 6.5.1 Photochemical Synthesis via Photosensitization 151
- 6.5.2 Photochemical Synthesis of Boranes and Their Derivatives 151
- 6.5.3 Synthesis of Chlorine Gas via Photolysis 152
- 6.5.4 Photochemical Synthesis of Fluorides 152
- 6.5.5 Photochemical Synthesis of H_2O_2 152
- 6.6 Synthesis of Inorganic Thin Films via Photochemical Reactions 153
- 6.6.1 Laser-Assisted Thin Film Formation of Inorganic Materials 153
- 6.6.2 Film Formation via Solution Photochemical Deposition 156
- 6.7 Photochemical Synthesis of Nanomaterials 157
- 6.8 Production of H_2 via Photodecomposition of Water 158
- 6.9 Summary 160
- References 161
- 7. Chemical Vapor Deposition and Its Applications in Inorganic Synthesis** 167
- J.-T. Wang*
- 7.1 Brief History of Chemical Vapor Deposition 167
- 7.2 Technical Fundamentals of Chemical Vapor Deposition 169
- 7.2.1 Simple Pyrolysis Reaction 169
- 7.2.2 Reduction-Oxidation Depositions 170
- 7.2.3 Deposition Through Synthetic Reaction 170
- 7.2.4 Deposition Through Chemical Mass Transportation 170
- 7.2.5 Plasma Enhanced Chemical Vapor Deposition (PECVD or PCVD) 171
- 7.2.6 Atomic Layer Chemical Vapor Deposition (ALCVD or ALD) 171
- 7.3 Low-Pressure Chemical Vapor Deposition and Its Simulation Model 172
- 7.4 Activated Low-Pressure Chemical Vapor Deposition Diamond Syntheses 174
- 7.5 Modern Thermodynamic Coupling Model of Chemical Vapor Deposition Diamond Syntheses 177
- 7.6 Nondissipative Thermodynamics and Nonequilibrium Phase Diagrams 179
- 7.7 Dissipative Thermodynamics and Chemical Oscillations 183
- 7.8 A Complete Basic Discipline of Thermodynamics 185
- 7.9 A New Statement of the Second Law of Thermodynamics 186
- References 187

8. Synthesis of Coordination Compounds and Coordination Polymers 189

M.-L. Tong, X.-M. Chen

- 8.1 Introduction to Coordination Compounds and Coordination Polymers 189
 - 8.1.1 Brief History of Coordination Compounds 189
 - 8.1.2 Brief History and Definition of Coordination Polymers 190
 - 8.1.3 Nets of Coordination Polymers 190
- 8.2 Synthetic Methods of Coordination Compounds 190
 - 8.2.1 Conventional Methods 190
 - 8.2.2 Nonconventional Method 191
 - 8.2.3 New Synthetic Methods 192
- 8.3 Rational Synthesis of Coordination Compounds 193
 - 8.3.1 Metalloligand Approach 193
 - 8.3.2 "Compartmentalized Ligand" Approach 194
 - 8.3.3 Templating Approach 195
 - 8.3.4 Substituent Reaction Approach 197
 - 8.3.5 Chiral Resolution 198
- 8.4 Molecular Design of Coordination Polymers 199
 - 8.4.1 Molecular Assembly 199
 - 8.4.2 Single Metal Noded Nets 199
 - 8.4.3 Metal-Cluster Noded Nets 201
 - 8.4.4 Pillared-Layer Nets 205
- 8.5 Structural Modulation of Coordination Polymers by Reaction Conditions 205
 - 8.5.1 Temperature Effect 206
 - 8.5.2 pH Effect 207
 - 8.5.3 Template and Additive Effect 208
 - 8.5.4 Solvent Effect 210
 - 8.5.5 Counter-Ion Effect 210
 - 8.5.6 In Situ Metal/Ligand Reactions 211
- 8.6 Postsynthetic Modification of Porous Coordination Polymers 212
 - 8.6.1 Metal Site Modification 213
 - 8.6.2 Organic Ligand Modification 214
- References 215

9. Cluster Compounds 219

G.-Y. Yang, D.-G. Huang

- 9.1 Description of the Clusters 219
 - 9.1.1 Definition of a Cluster and the Clusters 219
 - 9.1.2 Classification of the Clusters 219
 - 9.1.3 The Oxo Clusters 219
- 9.2 Synthesis of the Oxo Transition Metal Clusters Under Hydrothermal Conditions 220
 - 9.2.1 Substituted Synthesis on Polyoxometalate Cages 220
 - 9.2.2 Lacunary Directing Synthesis via the Lacunary Sites of Polyoxometalate Fragments 221
 - 9.2.3 Synergistic Directing Synthesis via Two or More Lacunary XW_9 Fragments 222
 - 9.2.4 Designed Synthesis via the Peripheral Substitution of Ni_6PW_9 Structural Building Units 225
- 9.3 Synthesis of the Oxo Lanthanide Clusters Under Hydrothermal Conditions 226
 - 9.3.1 Induced Synthesis via the Ligands 227
 - 9.3.2 Synergistic Coordination Between the First and Secondary Ligands 228
- 9.4 Synthesis of the Oxo Main Group Clusters Under Hydrothermal Conditions 229
 - 9.4.1 Templated Synthesis of Borates 229
 - 9.4.2 Templated Synthesis of Germanates and Borogermanates 231
 - 9.4.3 Self-Polymerization and Induced Congregation of Lanthanide Germanate Clusters 232
- 9.5 Synthesis of the Chalcogenide Clusters Under Hydro(solvo)thermal Conditions 233
 - 9.5.1 Tetrahedral Clusters 233
 - 9.5.2 T_n Clusters 233
 - 9.5.3 P_n Clusters 234
 - 9.5.4 C_n Clusters 234

- 9.5.5 Other Types of Supertetrahedral Clusters 234
- 9.5.6 Open-Framework Chalcogenides Made From Different Tetrahedral Clusters 234
- 9.5.7 Open-Framework Chalcogenides Based on Tetrahedral Clusters and Organic Linkers 234
- 9.6 **Synthesis of the Iron–Sulfur Clusters 235**
 - 9.6.1 Iron–Sulfur Clusters 235
 - 9.6.2 Mo(V)–Fe–S(Se) Clusters 236
 - 9.6.3 Heteroligated Mo(W)–Fe–S(Se) Clusters 238
 - 9.6.4 Carbon Monoxide Dehydrogenase 238
- 9.7 **Synthesis of the Metal Carbonyl Clusters 239**
 - 9.7.1 Metal Carbonyl Clusters 240
 - 9.7.2 Mixed-Metal Carbonyl Clusters 242
- References 242

10. Synthesis of Organometallic Compounds 247

J.K.C. Abbott, B.A. Smith, T.M. Cook, Z.-L. Xue

- 10.1 **Synthetic Reactions 248**
 - 10.1.1 Ligand Substitution 248
 - 10.1.2 Oxidative Addition and Reductive Elimination 249
 - 10.1.3 Insertion and Elimination 251
 - 10.1.4 Nucleophilic and Electrophilic Attack on Coordinated Ligands 254
 - 10.1.5 Reactions of Metal Vapors With Ligands or Ligand Precursors 259
- 10.2 **Preparation of Typical Organometallic Compounds 259**
 - 10.2.1 Metal Carbonyls 259
 - 10.2.2 Complexes With M–C σ Bonds 261
 - 10.2.3 Complexes With M–C Multiple Bonds 262
 - 10.2.4 Metal Hydrides 268
 - 10.2.5 π Complexes 269
 - 10.2.6 Paramagnetic Complexes 272
- 10.3 **Experimental Techniques 273**
- References 275

11. Synthesis and Assembly Chemistry of Inorganic Polymers 279

X.-Z. Tang, X.-B. Huang

- 11.1 **Polyphosphazenes 279**
- 11.2 **Synthesis of Novel Phosphazenes Compounds 280**
 - 11.2.1 Micro-Crosslinked Polyphosphazenes 280
 - 11.2.2 Star-Shaped Polyphosphazenes 282
 - 11.2.3 Penta-Armed Polyphosphazenes 282
 - 11.2.4 Polyphosphazenes With Nonlinear Optical Properties 285
 - 11.2.5 Phosphazene Separation Membranes 285
 - 11.2.6 Phosphazene-Modified Polyurethane 286
- 11.3 **Synthesis and Assembly Chemistry of Cyclophosphazene 287**
 - 11.3.1 In Situ Template Method 289
 - 11.3.2 Self-Assembly of Primary Particles 289
 - 11.3.3 Surface Polymerization on the Nano- or Microparticles 290
 - 11.3.4 Functional Polyphazene Nanomaterials 292
- 11.4 **Applications of Cyclomatrix Polyphosphazene Nanomaterials 298**
 - 11.4.1 Phosphazene Solid Polymer Electrolytes 298
 - 11.4.2 Precursor for Heteroatom-Doped Carbon Materials 301
- References 304

12. Soft Inorganic Supramolecular Systems 307

L.-X. Wu

- 12.1 **General Concepts and Methodology 307**
 - 12.1.1 Isolated Polyoxometalate Clusters 307
 - 12.1.2 Self-Assembly of Naked POMs in Solutions 308

- 12.1.3 The Self-Assembly of Organic Group Covalently Modified POMs in Solutions 309
- 12.1.4 Phase Transfer and Supported Building Blocks 311
- 12.1.5 Other Clusters 311
- 12.2 Assembly of POM Complexes in Solutions 311**
 - 12.2.1 Self-Assembly of Covalently Modified Clusters Assisting by Organic Counterions 311
 - 12.2.2 Assembly of POM Electrostatic Complexes in Hydrophobic Solvent Systems 312
 - 12.2.3 Assembly of Electrostatic POM Complexes in Hydrophilic Solvent Systems 313
 - 12.2.4 Inorganic–Organic Supramolecular Gels 314
- 12.3 The Assembly of POMS in Polymers 316**
 - 12.3.1 Covalent Connection of POMs With Polymer Chains 316
 - 12.3.2 Supramolecular Combination of POMs With Polymers 317
 - 12.3.3 Dispersion in Polymers 318
- 12.4 Assembly of POMS on Surfaces 320**
 - 12.4.1 The Adsorption of POM Clusters on Solid Surface 320
 - 12.4.2 Cluster/Particle Supported Pattern Formation 321
 - 12.4.3 Cluster-Patterned Surface for Domain Reactions 321
 - 12.4.4 Pattern Formation From Extended Clusters and Particles 321
- 12.5 Assembly of POMS in Liquid Crystals 322**
 - 12.5.1 Introduction of Clusters Into Liquid Crystals 323
 - 12.5.2 Assembly in Lyotropic Liquid Crystals 324
 - 12.5.3 Self-Assembly in Thermotropic Liquid Crystals 325
- References 327

13. Nonstoichiometric Compounds 329

J.-L. Zhang, G.-Y. Hong

- 13.1 Introduction to Nonstoichiometric Compounds 330**
 - 13.1.1 Definition 330
 - 13.1.2 Classification 331
 - 13.1.3 Point Defects in the Nonstoichiometric Compounds 331
- 13.2 Synthesis of Nonstoichiometric Compounds 333**
 - 13.2.1 Formation Mechanism 333
 - 13.2.2 Phase Diagram 335
 - 13.2.3 Synthesis Methods 337
- 13.3 Characterization of Nonstoichiometric Compounds 351**
 - 13.3.1 Composition Analysis 351
 - 13.3.2 Structure Determination 351
 - 13.3.3 Defect Detection 352
- References 352

14. Inorganic Synthesis of Actinides 355

W.-Q. Shi, L. Mei, Z.-F. Chai

- 14.1 The Oxidation State and Coordination Number of Actinides 355**
- 14.2 Actinide Coordination Compounds 356**
 - 14.2.1 Inorganic Actinide Compounds 356
 - 14.2.2 Actinide–Organic Compounds 361
- 14.3 Actinide-Based Nanomaterials 371**
 - 14.3.1 Actinide Oxide/Hydroxide Nanostructures 371
 - 14.3.2 Actinide-Containing Hybrid Nanomaterials 375
 - 14.3.3 Actinyl Peroxide Cage Clusters 377
- 14.4 Fabrication of Nuclear Fuels 378**
 - 14.4.1 Fabrication of Metal Fuel 378
 - 14.4.2 Fabrication of Dispersion Fuel 379
 - 14.4.3 Fabrication of Ceramic Fuel 380
- 14.5 Concluding Remarks 382**
- Acknowledgments 382
- References 382

15. Synthetic Chemistry of the Inorganic Ordered Porous Materials 389

Z.-A. Qiao, Q.-S. Huo

- 15.1 Porous Materials 389
- 15.2 Zeolite and Its Structure 390
 - 15.2.1 Basic Structural Unit of the Zeolite 390
 - 15.2.2 Framework Structure of Zeolite and Molecular Sieve 391
 - 15.2.3 Intergrowth in Zeolite 392
 - 15.2.4 The Composition of Zeolite and Molecular Sieve 392
- 15.3 The Synthesis of Zeolite 393
 - 15.3.1 Hydrothermal Zeolite Synthesis 393
 - 15.3.2 Zeolite Crystallization and Formation Mechanism 393
 - 15.3.3 Optimization of Zeolite Synthesis 394
- 15.4 Zeotype: Zeolite-Like Materials 395
 - 15.4.1 The Pure Silica Molecular Sieves and Clathrasil Compounds 395
 - 15.4.2 Aluminophosphate and Other Phosphate Molecular Sieves 395
 - 15.4.3 Organic-Inorganic Hybrid Zeolite and Microporous AlPO 396
- 15.5 New Strategies and New Trends of Zeolite Synthesis 396
 - 15.5.1 Ultra-Large Pore Zeolites and Zeolite-Like Materials 396
 - 15.5.2 Large Crystal 397
 - 15.5.3 Nanocrystal 397
 - 15.5.4 Phase Transition 398
 - 15.5.5 Nonaqueous Synthesis: Solvothermal, Ionothermal, Dry Gel Systems, and Solvent-Free Synthesis 399
 - 15.5.6 Mesoporous Zeolites 400
 - 15.5.7 F^- as Mineralizer 400
- 15.6 Basics of Ordered Mesoporous Materials 400
- 15.7 Understanding the Synthesis of Mesoporous Materials 402
 - 15.7.1 Synthetic System 402
 - 15.7.2 Formation Mechanism of Mesostructure: Liquid Crystal Template and Cooperative Self-Assembly 402
 - 15.7.3 Interaction Between Organic Template and Inorganic Species 403
 - 15.7.4 The Surfactant Packing Parameter 403
- 15.8 Typical Mesostructures and Mesoporous Materials 404
 - 15.8.1 2D Hexagonal Structure: MCM-41, SBA-15, FSM-16, and SBA-3 404
 - 15.8.2 Cubic Channel Mesostructures: MCM-48, FDU-5, and Im-3m Materials 405
 - 15.8.3 Cubic Caged Structures 405
 - 15.8.4 Deformed Mesophases, Low Ordered Mesostructures, and Other Possible Mesophases 407
 - 15.8.5 Siliceous Mesostructured Cellular Foams (MCFs) 407
 - 15.8.6 New Mesostructure 407
- 15.9 Synthesis Strategies for Mesoporous Silica 407
 - 15.9.1 Template 407
 - 15.9.2 Organic Additives 409
 - 15.9.3 Pore Size Control 409
 - 15.9.4 Post-Synthesis Hydrothermal Treatment 409
 - 15.9.5 Stabilization of Silica Mesophases 410
 - 15.9.6 Synthesis Through Acid-Base Pair 410
 - 15.9.7 Evaporation-Induced Self-Assembly (EISA) Process 410
 - 15.9.8 Chemical Modification: Grafting and Co-Condensation 411

- 15.9.9 Periodic Mesoporous Organosilicas (PMOs) 411
- 15.9.10 Nanocasting 411
- 15.10 New Compositions: Non-Silica-Based Mesoporous Materials 412**
 - 15.10.1 Metal Oxides and Other Inorganic Materials 412
 - 15.10.2 Mesoporous Polymer 414
 - 15.10.3 Other Mesoporous Materials 414
- 15.11 Morphology Control in Mesoporous Materials 416**
 - 15.11.1 Thin Film 417
 - 15.11.2 Fiber and Rod 417
 - 15.11.3 Monolith 417
- 15.12 Mesoporous Nanomaterials 417**
 - 15.12.1 Silica-Based Mesoporous Nanomaterials 417
 - 15.12.2 Mesoporous Carbon Nanomaterials 420
 - 15.12.3 Mesoporous Metal Oxide Nanomaterials 420
- 15.13 Porous Carbon Materials 421**
 - 15.13.1 Microporous Carbons 422
 - 15.13.2 Mesoporous Carbon Materials 422
- 15.14 Challenges for Porous Material Scientist 423**
References 424

16. Carbon Materials 429

S.-X. Xiao, C.-S. Huang, Y.-L. Li

- 16.1 Zero-Dimensional Carbon: Fullerene-Based Materials 429**
 - 16.1.1 Chemical Functionalization of Pristine Fullerenes 430
 - 16.1.2 Endohedral Fullerenes 433
 - 16.1.3 Heterofullerenes 435
 - 16.1.4 Potential Application of Fullerenes: PCBM-Polymer Systems for Solar Energy Conversion 435
- 16.2 One-Dimensional Carbon: Carbon Nanotubes 436**
 - 16.2.1 The History and Definition of CNTs 436
 - 16.2.2 Synthesis of CNTs 436
 - 16.2.3 Exciting Properties of CNTs 439

- 16.2.4 Potential Applications of CNTs 441
- 16.2.5 Conclusion and Perspectives 441
- 16.3 Two-Dimensional Carbon: Graphene-Based Materials 442**
 - 16.3.1 Introduction 442
 - 16.3.2 Preparation of Graphene 444
 - 16.3.3 Chemical Functionalization of Pristine Graphene 448
 - 16.3.4 Applications of Graphene 452
 - 16.3.5 Future Perspectives 452
- 16.4 2D Carbon: Graphdiyne and Graphyne-Based Materials 452**
 - 16.4.1 Introduction 452
 - 16.4.2 Experimental Efforts to Synthesize Graphdiyne 453
 - 16.4.3 Potential Application of Graphdiyne and Graphynes 453
 - 16.4.4 Future Perspectives 456
- References 456

17. Advanced Ceramic Materials 463

J.-K. Guo, J. Li, H.-M. Kou

- 17.1 Nanoceramics 463**
 - 17.1.1 Preparation of Nanoscaled Powders 463
 - 17.1.2 Sintering of Nanoceramics 466
- 17.2 Ceramic Matrix Composites (CMCs) 469**
 - 17.2.1 Fiber-Reinforced Ceramic Matrix Composites 469
 - 17.2.2 Whisker-Reinforced Ceramic Matrix Composites 473
 - 17.2.3 Particle Dispersion-Strengthened Ceramic Matrix Composites 473
 - 17.2.4 In Situ Growth Ceramic Matrix Composites 475
 - 17.2.5 Ceramic Nanocomposites 476
- 17.3 Integration of Structures and Functions 476**
 - 17.3.1 CNTs/SiO₂ Composites 476
 - 17.3.2 CNTs/BaTiO₃ Composites 476

- 17.4 **Transparent Ceramics** 478
 - 17.4.1 Optical Ceramic for Windows 478
 - 17.4.2 Laser Ceramics 481
 - 17.4.3 Upconversion Nanoparticles and Ceramics 484
 - 17.4.4 Ceramic Scintillators 485
 - References 487

18. Functional Host–Guest Materials 493

Assembly Chemistry of Anion-Intercalated Layered Materials 493

X. Duan, J. Lu, D.G. Evans

Introduction 493

- 18.1 **Structure of Anion-Intercalated Layered Materials** 494
 - 18.1.1 Introduction to Layered Double Hydroxides 494
 - 18.1.2 Structure of LDHs 494
 - 18.1.3 Metal Ions in LDH Layers 495
 - 18.1.4 Interlayer Anions of LDHs 497
- 18.2 **Preparative Chemistry of Anion-Intercalated Layered Materials** 498
 - 18.2.1 Methods of Preparation of LDHs 498
 - 18.2.2 Control of the Chemical Composition of LDHs 502
 - 18.2.3 Control of Mesomorphology of LDHs 504
 - 18.2.4 Control of the Macromorphology of LDHs 504
 - 18.2.5 Fabrication of LDH Films 507
- 18.3 **Assembly Chemistry of Anion-Intercalated Layered Materials** 512
 - 18.3.1 Intercalation–Assembly Concepts 512
 - 18.3.2 LDHs as Molecular Containers, Reactors, and 2D Interaction Space 513
 - 18.3.3 Summary 517
 - References 517

Assembly Chemistry of Porous Host–Guest Materials 524

X. Wei, J.-S. Chen

- 18.4 **Metal Clusters in Zeolites** 524
 - 18.4.1 Alkali Metal Clusters Encapsulated Within Zeolites 524

- 18.4.2 Noble Metal Clusters Encapsulated Within Porous Host 526
- 18.4.3 Transition Metal Clusters Encapsulated Within Porous Host 526

18.5 Semiconductor Nanoparticles in Porous Materials 527

18.6 Carbonaceous Materials in Porous Materials 529

- 18.6.1 Preparation of Carbonaceous Materials in Porous Supports 529
- 18.6.2 Fullerenes in Micro-/Mesoporous Molecular Sieves 529
- 18.6.3 Carbon Nanotubes Grown in Porous Materials 530

18.7 Polymers in Porous Matrix 532

- 18.7.1 Polymers in Microporous Zeolites 532
- 18.7.2 Polymerization in Mesoporous Materials 532
- 18.7.3 Polymerization in Porous Coordination Polymers 533

18.8 Metal Complexes Assembled Inside Porous Materials 533

- 18.8.1 Incorporation of Metal–Pyridine Ligand Complexes 534
- 18.8.2 Incorporation of Metal–Schiff Base Ligand Complexes 535
- 18.8.3 Incorporation of Porphyrin and Phthalocyanine Complexes 536
- 18.8.4 Encapsulation of Other Metal Complexes 537

18.9 Functional Compounds in Porous Host 538

- 18.9.1 Encapsulation of Dyes in Porous Host 538
- 18.9.2 Fluorescent Species in Porous Host 540
- 18.9.3 Porous Host for Drug Delivery 540

References 541

19. Hierarchical Materials 545

Y. Xu

19.1 Introduction to Hierarchical Materials 545

- 19.1.1 Innovation Inspired by Nature 545

19.1.2	Definition of Hierarchical Materials	545
19.1.3	Synthesis of Hierarchical Materials: From Art to Function-Led Design	546
19.2	Synthetic Strategies for Hierarchical Materials	547
19.2.1	Templating Strategy	547
19.2.2	Self-Formation Strategy	557
19.2.3	Bioinspired Strategy	560
19.2.4	Biomimetic Strategy	568
19.3	Concluding Remarks	570
	References	571
20.	Functional Crystals	575
	<i>N. Ye, J.-Y. Wang, R.I. Boughton, M.-C. Hong</i>	
20.1	Introduction	575
20.1.1	Natural and Synthetic Crystals	575
20.1.2	Classification and Applications of Functional Crystals	576
20.2	Fundamentals of Crystal Growth	576
20.2.1	Phases and Phase Diagrams	576
20.2.2	Driving Force in Crystal Growth	579
20.2.3	Nucleation	579
20.2.4	Interface of Crystal Growth	581
20.2.5	Transport During Crystal Growth	583
20.3	Crystal Growth Technology	585
20.3.1	Classification of Crystal Growth Methods	585
20.3.2	Crystal Growth from Vapor	586
20.3.3	Solution Growth	587
20.3.4	Flux Growth	589
20.3.5	Melt Growth	590
20.4	Some Important Functional Crystals	594
20.4.1	Laser Crystals	594
20.4.2	Nonlinear Optical Crystals	597
20.4.3	Electro-Optical Crystals	600
20.4.4	Scintillation Crystals	602
20.4.5	Relaxor Ferroelectric Single Crystals	603
20.4.6	Substrate Crystals	604
20.5	Discussion and Conclusion	608
	References	610

21. Synthetic Chemistry of Nanomaterials 613

S.-Z. Qiao, J. Liu, G.Q. Max Lu

21.1	Basics of the Synthetic Chemistry of Nanomaterials	613
21.2	Synthetic Method for Nanomaterials	614
21.2.1	Top-Down Methods	614
21.2.2	Bottom-Up Methods	617
21.2.3	Special Synthetic Method for Nanomaterials	623
21.3	Synthesis of Nanomaterials	624
21.3.1	Gold and Silver Nanocrystals	624
21.3.2	Magnetic Nanoparticles	625
21.3.3	Semiconductor Nanowires and Ultrathin Nanowires	626
21.3.4	Single Nanocrystals With a Large Percentage of Reactive or High-Energy Facets	628
21.3.5	Hollow Porous Nanostructures	629
21.3.6	Silica-Coated Core-Shell Nanostructures	634
21.4	Concluding Remarks	636
	References	636

22. Amorphous Materials 641

Z.-Q. Hu, A.-M. Wang, H.-F. Zhang

22.1	Amorphous Structure	641
22.1.1	Morphology of Noncrystal	641
22.1.2	Long-Range Disorder of Noncrystal	642
22.1.3	Molecular Dynamics Computer Simulation	643
22.2	Formation Rule of Amorphous Alloy	645
22.2.1	Principles for Formation of Amorphous Alloy	645
22.2.2	Semiempirical Criteria of Metallic Glass Formation	648
22.2.3	Criterion of Thermodynamic T_0 Curve	651
22.3	Preparation Technology of Amorphous Materials	653
22.3.1	Melt Quenching	653
22.3.2	Atomization	654
22.3.3	Laserglazing	655

- 22.3.4 Emulsion Droplet Method 656
 - 22.3.5 Mechanic Method 657
 - 22.3.6 Solid-State Reaction Method 658
 - 22.3.7 Radiation Method 659
 - 22.4 **Bulk Amorphous Alloy and Amorphous Alloy-Based Composite Materials 661**
 - 22.4.1 Bulk Amorphous Alloys 661
 - 22.4.2 Bulk Amorphous Alloy Matrix Composites 663
 - References 666
- 23. Preparation Chemistry of Inorganic Membranes 669**
- X.-L. Ma, J.Y.-S. Lin*
- 23.1 Inorganic Membranes and Their Major Characteristics 669
 - 23.2 Synthesis of Amorphous Microporous Inorganic Membranes 670
 - 23.2.1 Silica Membranes With Improved Stability and Controllable Pore Size 670
 - 23.2.2 Thin Carbon Molecular Sieve Membranes 671
 - 23.3 Synthesis of Crystalline Microporous Inorganic Membranes 674
 - 23.3.1 Zeolite Membranes With Minimized Intercrystalline Defects 674
 - 23.3.2 MOF Membranes 679
 - 23.3.3 Nanosheet-Packed Molecular Sieve Membranes 681
 - 23.4 Conclusions 684
 - Acknowledgments 685
 - References 685
- 24. Frontier of Inorganic Synthesis and Preparative Chemistry (I) Biomimetic Synthesis 687**
- K.-S. Liu, D.-L. Tian, L. Jiang*
- 24.1 Introduction 687
 - 24.2 Biomineralization and Its Mimetic Inorganic Materials 687
 - 24.2.1 Introduction 687
 - 24.2.2 Biomineralization 689
 - 24.2.3 Diatoms and Their Mimetic Mineralization Materials 690
 - 24.2.4 Nacre and Its Mimetic Mineralization Materials 692
- 24.3 Biotemplated Inorganic Materials 695**
- 24.3.1 Introduction 695
 - 24.3.2 DNA 695
 - 24.3.3 Bacteria 699
 - 24.3.4 Insect Wings 700
 - 24.3.5 Shell Membranes 702
 - 24.3.6 Other Typical Biotemplates 702
- 24.4 Biomimetic Synthesis of Inorganic Chiral Materials 702**
- 24.4.1 Introduction 702
 - 24.4.2 Zeolites and Molecular Sieves 702
 - 24.4.3 SiO₂ 704
 - 24.4.4 Metals 705
 - 24.4.5 Others 706
- 24.5 Bioinspired Multiscale Inorganic Materials 706**
- 24.5.1 Introduction 706
 - 24.5.2 Bioinspired Surfaces With Special Wettability 707
 - 24.5.3 Biomimetic Hollow Micronanomaterials 710
 - 24.5.4 High-Performance Organic-Inorganic Composites Inspired by Nacre 710
 - 24.5.5 Others 712
 - References 713
- 25. Frontier of Inorganic Synthesis and Preparative Chemistry (II)-Designed Synthesis—Inorganic Crystalline Porous Materials 723**
- J.-H. Yu, J.-Y. Li*
- 25.1 Structure Design of Inorganic Crystalline Porous Materials 724
 - 25.1.1 Design of Zeolite Structures With Predefined Pore Geometries 724
 - 25.1.2 Structure Design With Predefined Structural Building Units and Double-Layer Silica Sheets 728
 - 25.2 Evaluation of Chemical Feasibility of Zeolite Structures 736
 - 25.2.1 Predicting Structural Feasibility of Pure-Silica Zeolites 736
 - 25.2.2 Predicting Structural Feasibility of Silica and Germania Zeolites 738
 - 25.2.3 Flexibility as an Indicator of Feasibility of Zeolite Frameworks 740

25.2.4	Criteria for Feasible Zeolite Frameworks for Target Synthesis	740	25.4	Synthesis Guided by Topotactic Transformation	756
25.3	Attempts to the Rational Synthesis of Inorganic Porous Crystalline Materials	742	25.5	Future Perspectives on the Tailor-Made Synthesis of Desired Inorganic Porous Crystalline Materials	758
25.3.1	Synthesis Guided by the Structure-Directing Effect of Template	743	25.6	Concluding Remarks	759
25.3.2	Synthesis Guided by Substituent Element Effects	749		References	759
25.3.3	Synthesis Guided by Data Mining	753			

Index	763
-------	-----