

Contents

	Preface	<i>ix</i>
	Acknowledgements	<i>xi</i>
	Abbreviations	<i>xv</i>
1	Introduction	<i>1</i>
2	Solid-State Reactions	<i>5</i>
2.1	Reactions Between Solid Compounds	<i>5</i>
2.1.1	Ceramic Method	<i>5</i>
2.1.1.1	General Aspects of Solid-State Reactions	<i>8</i>
2.1.1.2	Facilitating Solid-State Reactions	<i>12</i>
2.1.2	Mechanochemical Synthesis	<i>16</i>
2.1.3	Carbothermal Reduction	<i>17</i>
2.1.4	Combustion Synthesis	<i>22</i>
2.1.4.1	Solution Combustion Synthesis	<i>29</i>
2.2	Solid–Gas Reactions	<i>31</i>
2.3	Ceramics Processing	<i>34</i>
2.3.1	Sintering	<i>38</i>
2.4	Intercalation Reactions	<i>41</i>
2.4.1	Mechanistic Aspects	<i>47</i>
2.4.2	Preparative Methods	<i>49</i>
2.4.3	Intercalation of Polymers in Layered Systems	<i>51</i>
2.4.4	Pillaring of Layered Compounds	<i>52</i>
	Further Reading	<i>55</i>
3	Formation of Solids from the Gas Phase	<i>57</i>
3.1	Chemical Vapour Transport	<i>57</i>
3.1.1	Halogen Lamps	<i>59</i>
3.1.2	Transport Reactions	<i>63</i>
3.2	Chemical Vapour Deposition	<i>65</i>
3.2.1	General Aspects	<i>65</i>
3.2.2	Techniques	<i>73</i>
3.2.3	Metal CVD	<i>78</i>
3.2.3.1	Silicon and Aluminium	<i>79</i>

3.2.3.2	Tungsten	82
3.2.3.3	Copper	83
3.2.4	CVD of Carbon	86
3.2.5	CVD of Binary and Multinary Compounds	89
3.2.5.1	Metal Oxides	90
3.2.5.2	Metal Nitrides	92
3.2.5.3	Metal Chalcogenides and Pnictides	95
3.2.6	Aerosol-Assisted CVD	97
3.2.7	Chemical Vapour Infiltration	99
3.3	Gas-Phase Powder Syntheses	101
	Further Reading	110
4	Formation of Solids from Solutions and Melts	113
4.1	Glass	113
4.1.1	The Structural Theory of Glass Formation	115
4.1.2	Crystallization Versus Glass Formation	118
4.1.3	Glass Melting	123
4.1.4	Phase Separation	127
4.1.5	Metallic Glasses	128
4.2	Crystallization from Solution	132
4.2.1	Monodispersity	133
4.2.2	Shape Control of Crystals	135
4.2.3	Non-classical Crystallization	137
4.2.4	Biom mineralization	140
4.2.4.1	Biogenic Materials	140
4.2.4.2	Biom mineralization	146
4.2.4.3	Bioinspired Materials Chemistry	151
4.3	Electrodeposition	156
4.3.1	Colloids	156
4.3.2	Electrodeposition of Ceramics	159
4.4	Solvothermal Processes	161
4.4.1	Fundamentals	161
4.4.2	Growing Single Crystals	165
4.4.3	Solvothermal Synthesis	168
4.4.3.1	Metal Oxides	169
4.4.3.2	Synthetic Calcium Phosphate Biomaterials	171
4.4.3.3	Zeolites	172
4.5	Sol–Gel Processes	177
4.5.1	The Chemistry of Alkoxide Precursors	181
4.5.2	Hydrolysis and Condensation	185
4.5.2.1	Silica-Based Materials	186
4.5.2.2	Metal Oxide-Based Materials	192
4.5.3	The Sol–Gel Transition (Gelation)	195
4.5.4	Aging and Drying	201
4.5.5	Nonhydrolytic Sol–Gel Processes	203
4.5.6	Inorganic–Organic Hybrid Materials	204
4.5.7	Aerogels	208
	Further Reading	214

5	Preparation and Modification of Inorganic Polymers	217
5.1	General Aspects	218
5.1.1	Synthesis and Crosslinking	219
5.1.2	Copolymers	221
5.2	Polysiloxanes (Silicones)	222
5.2.1	Properties and Applications	222
5.2.2	Structure	226
5.2.3	Preparation	227
5.2.4	Curing ('Vulcanizing')	231
5.3	Polyphosphazenes	233
5.3.1	Properties and Applications	233
5.3.2	Preparation and Modification	236
5.4	Polysilanes	239
5.4.1	Properties and Applications	239
5.4.2	Preparation	242
5.5	Polycarbosilanes	245
5.6	Polysilazanes and Related Polymers	249
5.7	Polymers with B–N Backbones	252
5.8	Other Inorganic Polymers	253
5.8.1	Other Phosphorus-Containing Polymers	254
5.8.2	Polymers with S–N Backbones	255
5.8.3	Metallopolymers	255
5.9	Polymer-to-Ceramic Transformation	258
	Further Reading	264
6	Self-Assembly	267
6.1	Self-Assembled Monolayers	268
6.2	Metal–Organic Frameworks	271
6.2.1	Modularity of the Structures	271
6.2.2	Synthesis and Modification	276
6.3	Supramolecular Arrangements of Surfactants and Block Copolymers	279
6.4	Layer-by-Layer Assembly	282
	Further Reading	285
7	Templating	287
7.1	Introduction to Porosity and High Surface Area Materials	289
7.2	Infiltration and Coating of Templates	292
7.2.1	Replica Technique	293
7.2.2	Sacrificial Templates	295
7.2.2.1	Colloidal Crystals	296
7.2.2.2	Hollow Particles	298
7.2.3	Direct Foaming	300
7.2.4	Nanocasting	302
7.3	<i>In Situ</i> Formation of Templates	305
7.3.1	Breath Figures	305
7.3.2	Freeze Casting	306
7.3.3	Supramolecular Assemblies of Amphiphiles	307

- 7.3.3.1 Synthesis of Periodic Mesoporous Silicas 310
- 7.3.3.2 Evaporation-Induced Self-Assembly 314
- 7.3.3.3 Incorporation of Organic Groups 315
- 7.4 Reorganization and Transformation Processes 317
 - 7.4.1 Pseudomorphic Transformation 317
 - 7.4.2 Kirkendall Effect 319
 - 7.4.3 Galvanic Replacement 320
 - 7.4.4 Phase Separation and Leaching 321
- Further Reading 325

8 Nanomaterials 327

- 8.1 Properties of Nanomaterials 329
 - 8.1.1 Properties Due to Surface Effects 329
 - 8.1.2 Properties of Nanocrystalline Materials 331
 - 8.1.3 Catalytic Properties 332
 - 8.1.4 Optical Properties 333
 - 8.1.5 Electrical Properties 336
 - 8.1.6 Magnetic Properties 337
- 8.2 Syntheses of Nanoparticles 339
 - 8.2.1 Severe Plastic Deformation 340
 - 8.2.2 Formation from Vapours 341
 - 8.2.3 Formation from Solution 343
 - 8.2.4 Surface Modification with Organic Groups 348
- 8.3 One-Dimensional Nanostructures 352
 - 8.3.1 Nanowires and Nanorods 352
 - 8.3.2 Nanotubes 357
 - 8.3.2.1 Carbon Nanotubes 357
 - 8.3.2.2 Titania Nanotubes 362
- 8.4 Two-Dimensional Nanomaterials 365
 - 8.4.1 Graphene 365
 - 8.4.2 Other 2D Nanomaterials 369
- 8.5 Heterostructures and Composites 370
 - 8.5.1 Core–Shell Nanoparticles 370
 - 8.5.2 Vertical 2D Heterostructures 373
 - 8.5.3 Polymer–Matrix Nanocomposites 374
 - 8.5.4 Supported Metal Nanoparticles 376
- Further Reading 378

Glossary 381

Index 389