

Contents

Foreword *xi*

Preface *xiii*

1	Introduction of the Metastable-Phase Materials	1
	<i>Qi Shao and Mingwang Shao</i>	
1.1	Introduction	1
1.2	What Are Metastable-Phase Materials?	1
1.3	The Categories of Metastable-Phase Materials	2
1.3.1	Different Packing Orders	3
1.3.2	Different Connecting Modes	3
1.3.3	Different Coordination Number	3
1.3.4	Different Kinds of Chemical Bonds	4
1.3.5	Order and Disorder Polymorphs	5
1.3.6	Molecular Thermal-Motion-Related Polymorphs	5
1.3.7	Spin-Related Polymorphs	6
1.4	The Influence on Polymorphs of Materials	6
1.4.1	Temperature	6
1.4.2	Pressure	6
1.4.3	The Stability in Nano-size Metastable-Phase Catalysts	7
1.5	The Wide Applications of Metastable-Phase Materials	8
1.6	The Criterion for Stable-Phase and Metastable-Phase Materials	8
	References	10
2	Synthetic Methodology	15
	<i>Qi Shao</i>	
2.1	Introduction	15
2.2	The Key for Synthesizing Metastable-Phase Materials	15
2.3	The Synthetic Methods for Synthesizing Metastable-Phase Materials	16
2.3.1	Mechanical-Energy-Related Methods	17
2.3.2	Thermal-Energy-Related Methods	18
2.3.2.1	Hydrothermal Method	18

- 2.3.2.2 Solvothermal Method 19
- 2.3.2.3 Rapid Solidification or Quenching 20
- 2.3.2.4 Reflux Methods 20
- 2.3.2.5 Other Methods Related with Thermal Energy 22
- 2.3.3 High Pressure 22
- 2.3.4 Soft Chemical Method 23
- 2.3.5 Other Methods 23
- 2.3.6 The Combination of These Methods 25
- References 25

3 Characterization 33

Qi Shao

- 3.1 Introduction 33
- 3.2 Characterizations 33
 - 3.2.1 X-ray Diffraction 33
 - 3.2.2 Transmission Electron Microscopy 36
 - 3.2.3 Synchrotron X-ray Absorption 38
 - 3.2.3.1 XANES 38
 - 3.2.3.2 EXAFS 38
 - 3.2.4 X-ray Photoelectron Spectroscopy 40
 - 3.2.5 Neutron Diffraction 41
 - 3.2.6 X-ray Magnetic Circular Dichroism (XMCD) 41
- 3.3 How to Determine the Phase of Metastable-Phase 2D Metal Oxides 43
- References 45

4 Metastable-Phase Metals 51

Qi Shao

- 4.1 Introduction 51
- 4.2 Noble Metals 51
 - 4.2.1 Au and Ag 51
 - 4.2.2 Pd and Rh 52
 - 4.2.3 Pt and Ir 55
 - 4.2.4 Ru and Os 57
- 4.3 Non-noble Metals 60
 - 4.3.1 Ni 60
 - 4.3.2 Co 62
 - 4.3.3 Fe 62
 - 4.3.4 Mn 62
 - 4.3.5 Sn 63
 - 4.3.6 W 64
- 4.4 The Criterion to Determine the Stable-Phase and Metastable-Phase Metals 64
- References 66

5	Metastable-Phase Oxide, Chalcogenide, Phosphide, and Boride Materials	71
	<i>Qi Shao</i>	
5.1	Introduction	71
5.2	Oxides	71
5.2.1	TiO ₂	71
5.2.2	Fe ₂ O ₃	73
5.2.3	ZnO	75
5.3	Chalcogenides	76
5.3.1	MoS ₂	76
5.3.2	CdS and ZnS	78
5.3.3	Cu ₂ SnSe ₃	78
5.4	Others	78
5.4.1	C	78
5.4.2	ZrP and HfP	79
5.4.3	Ni ₇ B ₃ and OsB ₂	79
	References	80
6	Spin-Dependent Metastable-Phase Materials	85
	<i>Qi Shao</i>	
6.1	Introduction	85
6.2	Spin-Related Catalysis	85
6.2.1	Background	85
6.2.2	OER	85
6.2.3	ORR	86
6.3	Spin-Related Catalysts for Alkaline OER	88
6.3.1	Spinel Oxides	88
6.3.2	Oxyhydroxide	88
6.4	Spin-Related Catalyst for Acidic OER	89
	References	90
7	Crystallography, Design, and Synthesis of Two-Dimensional Metastable-Phase Oxides	93
	<i>Mingwang Shao and Qi Shao</i>	
7.1	Introduction	93
7.2	The Point Group, Crystal System, Crystal Lattice, and Space Groups of 2D Materials	93
7.2.1	Background	93
7.2.2	Theoretical Deduction	96
7.2.2.1	The Determination of 2D Point Group	96
7.2.2.2	The Determination of 2D Crystal Systems	97
7.2.2.3	The Determination of Crystal Lattices	97
7.2.2.4	The Determination of 2D Space Group	98
7.3	The Possible Crystal Structures and Chemical Formula of 2D Metal Oxides	100

7.3.1	The Importance of 2D Metal Oxides	100
7.3.2	The Possible Crystal Structure of 2D Metal Oxides	101
7.3.2.1	CN of 3	102
7.3.2.2	CN of 4	104
7.3.2.3	CN of 5	104
7.3.2.4	CN of 6	105
7.3.2.5	CN of 7	106
7.3.2.6	CN of 8	107
7.3.2.7	CN of 9	108
7.3.2.8	CN of 10	108
7.3.2.9	CN of 11	108
7.3.2.10	CN of 12	108
7.3.3	The Possible Metallene Oxides	110
7.4	How to Prepare Metastable-Phase 2D Metal Oxides	119
7.5	2D Metastable-Phase Noble Metal Oxides	120
7.5.1	Introduction of 2D Metastable-Phase Noble Metal Oxides	120
7.5.2	2D Metastable-Phase Iridium Oxides	120
7.5.3	2D Metastable-Phase Platinum Oxides	120
7.5.4	2D Metastable-Phase Rhodium Oxides	123
7.5.5	2D Metastable-Phase Palladium Oxides	124
7.6	Metastable-Phase 2D Non-noble Metal Oxides	126
7.6.1	2D Metastable-Phase Cerium Oxide	126
7.6.2	2D Metastable-Phase Hafnium Oxide	127
7.6.3	2D Metastable-Phase Tin Oxide	127
7.7	The Covalent Bond Behavior in Metastable-Phase 1T Metal Oxides	129
7.7.1	The Relationship Between Bonds and Valences for Chemical Bonds	129
7.7.2	Distortion Theorem and Jahn–Teller Effect	130
7.7.3	The Behavior Against Distortion Theorem of 1T Oxides and Anti-Jahn–Teller Effect of 1T PdO ₂	131
7.7.4	The Origin of Flexibility for 1T Metal Oxides	132
	References	134
8	Electrocatalysis	141
	<i>Qi Shao</i>	
8.1	Introduction	141
8.2	Several Typical Electrochemical Reactions	141
8.2.1	Hydrogen Evolution Reaction	141
8.2.2	Oxygen Evolution Reaction	143
8.2.3	Oxygen Reduction Reaction	143
8.2.4	Carbon Dioxide Reduction Reaction	144
8.3	Metastable-Phase Catalysts for Advanced Electrocatalysis	145
8.3.1	Metastable-Phase Metals	145
8.3.2	Metastable-Phase Oxides	148
8.3.3	Metastable-Phase Transition Metal Chalcogenides	157
8.3.4	Metastable-Phase Phosphides	159

8.3.5	Metastable-Phase Carbides	161
	References	167
9	Photocatalysis	173
	<i>Mingwang Shao and Zhenhui Kang</i>	
9.1	Introduction	173
9.2	Fundamental Concepts of Photocatalysis	173
9.2.1	Mechanism of Photocatalysis	173
9.2.2	Experimental Parameters of Photocatalysis	174
9.2.3	How to Determine the Bandgap	175
9.2.4	The Change of Bandgap, CB, and VB of Nanomaterials	176
9.3	Metastable-Phase Catalysts and Photocatalysis	177
9.3.1	TiO ₂	177
9.3.2	TaON	178
9.3.3	MoO ₃	178
9.3.4	WO ₃	179
9.3.5	Bi ₂ O ₃	179
9.3.6	MoS ₂	179
9.3.7	MnS	181
9.3.8	FeVO ₄	181
9.3.9	Sr _{0.5} TaO ₃	181
9.3.10	Bi ₂₀ TiO ₃₂	181
9.3.11	Bi ₂ Zr ₂ O ₇	181
9.3.12	Bi ₂ SiO ₅	181
9.3.13	Ag ₂ MoO ₄	181
9.3.14	Ag ₂ WO ₄	182
9.3.15	ZnMoO ₄	182
9.3.16	K ₂ LaTa ₂ O ₆ N	182
9.3.17	ZrSnO ₄	182
9.3.18	(1-x)BiFeO _{3-x} PbTiO ₃	182
9.4	The Advantages and Disadvantages of Photocatalysis	182
	References	183
10	Thermocatalysts	191
	<i>Qi Shao</i>	
10.1	Introduction	191
10.2	Several Typical Thermocatalytic Reactions	191
10.2.1	Synthesis of Ammonia	191
10.2.2	Water-Gas Shift Reaction	192
10.2.3	Catalytic Reforming	192
10.2.4	Hydrogenation	192
10.2.5	CO Oxidation	192
10.2.6	Fischer-Tropsch Reaction	193
10.3	Metastable-Phase Catalysts for Thermocatalysis	193
10.3.1	MoO ₃ and MoO ₂	193

10.3.2	ZrO ₂	194
10.3.3	Al ₂ O ₃	195
10.3.4	CuO and Cu ₄ O ₃	195
10.3.5	FeO and Fe ₂ O ₃	195
10.3.6	Other Oxides	196
10.3.7	Metals and Alloys	198
10.3.8	Chalcogenides	199
10.3.9	Carbides	199
10.3.10	Borides	200
	References	201
	Summary and Outlook	207
	Index	209