

Contents

Abbreviations — V

Preface — VII

1 The Rare-Earth Elements — 1

1.1 An Introduction — 1

1.2 A Short History of Discovery — 3

Part I: General Aspects of Rare-Earth Elements

2 Basic Aspects and General Properties — 11

2.1 The Rare-Earth Elements in the Periodic Table — 11

2.2 Electronic Configuration — 16

3 General Trends of Physical and Chemical Behavior — 17

3.1 Atomic, Ionic and van der Waals Radii — 17

3.2 Densities, Melting and Boiling Points — 18

3.3 Crystal Structures of the Elements — 19

3.4 On Cerium—a Short Story — 21

3.5 Ionization Behavior and Chemical Hardness — 24

3.6 Oxidation States—Colors in an Aqueous Solution — 26

3.7 General Reactivity — 28

3.8 Solution Chemistry — 29

3.8.1 Reduction Potentials — 29

3.8.2 Acid-Base Chemistry and Simple Complexes — 31

4 Natural Resources — 36

4.1 General Aspects — 36

4.2 Ores and Minerals — 38

5 Production — 42

5.1 Concentration of Rare-Earth Minerals — 42

5.2 Separation and Purification of the Elements — 43

5.2.1 Solvent-Solvent Extraction — 45

5.2.2 Further Separation Approaches — 47

5.2.3 Scandium — 48

5.3 Obtaining the Elements — 49

6	Basic Compound Classes — 50
6.1	Hydrogen Compounds — 50
6.1.1	Structures and Bonding of RH_2 and RH_3 — 51
6.1.2	Hydrogen Storage— LaNi_5 — 54
6.2	Binary Halides and Halide Oxides — 56
6.2.1	Trihalides RX_3 — 57
6.2.2	Tetrafluorides RF_4 — 61
6.2.3	Reduced Halides — 62
6.2.4	Halide Oxides — 66
6.3	Oxides — 70
6.3.1	The Sesquioxides R_2O_3 and Mixed III/IV-Oxides — 70
6.3.2	Syntheses and Structures of the Dioxides and Intermediate Oxides — 72
6.3.3	A Closer Look On CeO_2 — 74
6.3.4	The Monoxides and Eu_3O_4 — 76
6.3.5	The Superconducting Oxides $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ And $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ — 77
6.4	Borides, Carbides, Nitrides and Sulfides — 78
6.4.1	Borides — 78
6.4.2	Carbides and Nitrides — 80
6.4.3	Sulfides — 82
6.5	Silicates And Selected Silicate-Analogous Compounds — 83
6.5.1	Coordination Strength — 83
6.5.2	Silicates — 84
6.5.3	Aluminates — 86
6.5.4	Nitridosilicates, Nitridoaluminates and Oxonitridosilicates — 88
6.5.5	Phosphates — 90
6.5.6	Borophosphates, Borosulfates and Fluorooxoborates — 91

Part II: Properties and Applications

7	Transitions — 97
7.1	Transition Probability — 97
7.2	Configuration, Terms and Levels — 97
7.3	Electric and Magnetic Dipole Transitions — 100
7.4	Spin Selection Rule — 102
7.5	Jablonski Diagrams — 103
7.6	Energy Transfer Mechanisms — 105
7.6.1	FRET Mechanism — 106
7.6.2	Dexter Mechanism — 106
7.7	Further Parameters — 107
7.7.1	Bandwidth of a Transition — 107
7.7.2	Thermal Quenching and Concentration Quenching — 108

- 7.7.3 Color Coordinates — **109**
- 7.7.4 Color Temperature — **110**
- 7.8 Transitions within a 4f Configuration—Judd–Ofelt Theory — **111**

8 Optical Properties — 117

- 8.1 Nephelauxetic Effect — **117**
- 8.2 Charge-Transfer Transitions — **119**
 - 8.2.1 General Aspects — **119**
 - 8.2.2 View on Rare-Earth Ions — **120**
 - 8.2.3 Optical Electronegativity — **122**
- 8.3 The Chemical Shift Model — **123**
- 8.4 Emitters Weakly Interacting With Ligands — **126**
 - 8.4.1 Gadolinium—Only Partially Innocent — **127**
 - 8.4.2 Terbium—Bright Green or Also Blue? — **130**
 - 8.4.3 Europium—Sometimes Hypersensitive — **134**
 - 8.4.4 Samarium and Burning Holes — **140**
 - 8.4.5 Dysprosium—As Long-Lasting as Possible — **142**
 - 8.4.6 Holmium—A Chameleon — **145**
 - 8.4.7 Erbium—Putting Photons Together — **147**
 - 8.4.8 Neodymium—A Perfect Match for Stimulated Emission — **150**
 - 8.4.9 Praseodymium—Occasionally a Knife for Photons — **153**
 - 8.4.10 Thulium—Normally Blue — **155**
 - 8.4.11 Ytterbium—Solar Cells are Pleased — **156**
- 8.5 Emitters Strongly Interacting With Ligands (5d–4f Transitions) — **158**
 - 8.5.1 Trivalent Cerium—the Most Efficient Ln^{3+} — **159**
 - 8.5.2 Divalent Europium—a True Chameleon — **164**
- 8.6 On White LEDs—a Short Story — **167**
- 8.7 Further Divalent Rare-Earth Ions — **171**

9 Magnetism — 174

- 9.1 Basic Principles — **174**
- 9.2 Paramagnetism — **177**
 - 9.2.1 Inner Transition Metals — **178**
 - 9.2.2 Van Vleck Paramagnetism — **180**
 - 9.2.3 Outer Transition Metals — **182**
- 9.3 Magnetic Ordering — **183**
 - 9.3.1 Ferromagnetism and Antiferromagnetism — **184**
 - 9.3.2 Magnetism of Metallic 4f Systems — **187**
- 9.4 Magnetic Behavior of the Lanthanide metals — **189**
- 9.5 The Europium Chalcogenides, Antiferromagnetism and Ferrimagnetism — **192**
- 9.6 Rare-Earth Ferromagnets—Often Really Hard and Permanent — **195**

9.6.1	SmCo_5 —	197
9.6.2	$\text{Sm}_2\text{Co}_{17}$ —	199
9.6.3	$\text{Sm}_2\text{Fe}_{17}\text{N}_3$ —	199
9.6.4	$\text{Nd}_2\text{Fe}_{14}\text{B}$ —	200
9.7	Magnetocaloric Materials —	201
9.7.1	$\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ —	203
9.7.2	Eu_2In —	204

Epilogue — 205

A Ionic Radii — 207

B Physical Properties — 209

C Chemical Shift Model Parameters — 211

D Structure Types Derived From Close Packings — 213

E Exemplary Calculation of the Transition Integral's Behavior — 217

F Excerpts of MAPLE Calculations — 219

F.1 Coordination and MAPLE of LaH_3 and GdH_3 — **219**

F.2 Coordinations in EuBr_2 — **226**

F.3 Coordinations in B Type Sm_2O_3 — **228**

General Index — 231

Formula Index — 237

Bibliography — 241