

Contents

Preface	xvii
Chemistry – Solid State Chemistry – Materials Chemistry – Materials Science and Engineering	xix
Companion Website	xxiii
Crystal Viewer	xxiii
Crystal Structure Library	xxiv
Biography	xxv
1 Crystal Structures and Crystal Chemistry	1
1.1 Unit Cells and Crystal Systems	1
1.2 Symmetry	3
1.2.1 Rotational Symmetry; Symmetry Elements and Operations	3
1.2.2 Quasicrystals	6
1.2.3 Mirror Symmetry	6
1.2.4 Centre of Symmetry and Inversion Axes	6
1.2.5 Point Symmetry and Space Symmetry	9
1.3 Symmetry and Choice of Unit Cell	10
1.4 Lattice, Bravais Lattice	11
1.5 Lattice Planes and Miller Indices	14
1.6 Indices of Directions	16
1.7 <i>d</i> -Spacing Formulae	17
1.8 Crystal Densities and Unit Cell Contents	17
1.9 Description of Crystal Structures	18
1.10 Close Packed Structures – Cubic and Hexagonal Close Packing	19
1.11 Relationship between Cubic Close Packed and Face Centred Cubic	21
1.12 Hexagonal Unit Cell and Close Packing	21
1.13 Density of Close Packed Structures	22
1.14 Unit Cell Projections and Atomic Coordinates	24
1.15 Materials That Can Be Described as Close Packed	25
1.15.1 Metals	25
1.15.2 Alloys	25
1.15.3 Ionic Structures	26

1.15.3.1	Tetrahedral and Octahedral Sites	26
1.15.3.2	Relative Sizes of Tetrahedral and Octahedral Sites	28
1.15.3.3	Location of Tetrahedral and Octahedral Sites in an <i>fcc</i> Unit Cell; Bond Length Calculations	29
1.15.3.4	Description of Crystal Structures; Fractional Atomic Coordinates	30
1.15.4	Covalent Network Structures	31
1.15.5	Molecular Structures	31
1.15.6	Fullerenes and Fullerides	31
1.16	Structures Built of Space-Filling Polyhedra	33
1.17	Some Important Structure Types	35
1.17.1	Rock Salt (NaCl), Zinc Blende or Sphalerite (ZnS), Fluorite (CaF ₂), Antifluorite (Na ₂ O)	35
1.17.1.1	Rock Salt Structure	37
1.17.1.2	Zinc Blende (Sphalerite) Structure	38
1.17.1.3	Antifluorite/Fluorite Structure	39
1.17.1.4	Bond Length Calculations	41
1.17.2	Diamond	42
1.17.3	Wurtzite (ZnS) and Nickel Arsenide (NiAs)	43
1.17.4	Caesium Chloride (CsCl)	47
1.17.5	Other AX Structures	48
1.17.6	Rutile (TiO ₂), Cadmium Iodide (CdI ₂), Cadmium Chloride (CdCl ₂) and Caesium Oxide (Cs ₂ O)	49
1.17.7	Perovskite (SrTiO ₃)	54
1.17.7.1	Tolerance Factor	57
1.17.7.2	BaTiO ₃	57
1.17.7.3	Tilted Perovskites: Glazer Notation	58
1.17.7.4	CaCu ₃ Ti ₄ O ₁₂ , CCTO	62
1.17.7.5	Anion-Deficient Perovskites	62
1.17.7.6	Stoichiometry–Property Relations	62
1.17.8	Rhenium Trioxide (ReO ₃), Perovskite Tungsten Bronzes, Tetragonal Tungsten Bronzes and Tunnel Structures	63
1.17.9	Spinel	66
1.17.10	Olivine	70
1.17.11	Corundum, Ilmenite and LiNbO ₃	72
1.17.12	Fluorite-Related Structures and Pyrochlore	72
1.17.13	Garnet	75
1.17.14	Perovskite-Rock Salt Intergrowth Structures: K ₂ NiF ₄ , Ruddlesden–Popper Phases and Layered Cuprate Superconductors	76
1.17.15	The Aluminium Diboride Structure (AlB ₂)	80
1.17.16	Silicate Structures – Some Tips to Understanding Them	81
2	Crystal Defects, Non-Stoichiometry and Solid Solutions	83
2.1	Perfect and Imperfect Crystals	83
2.2	Types of Defect: Point Defects	84
2.2.1	Schottky Defect	85
2.2.2	Frenkel Defect	85
2.2.2.1	The Kroger–Vink Notation for Crystal Defects	86
2.2.2.2	Thermodynamics of Schottky and Frenkel Defect Formation	87

2.2.3	Colour Centres	90
2.2.4	Vacancies and Interstitials in Non-Stoichiometric Crystals: Extrinsic and Intrinsic Defects	91
2.2.5	Defect Clusters or Aggregates	92
2.2.6	Interchanged Atoms: Order–Disorder Phenomena	95
2.3	Solid Solutions	95
2.3.1	Substitutional Solid Solutions	96
2.3.2	Interstitial Solid Solutions	98
2.3.3	More Complex Solid Solution Mechanisms: Aliovalent Substitution	99
2.3.3.1	Ionic Compensation Mechanisms	99
2.3.3.2	Electronic Compensation: Metals, Semi- and Superconductors	102
2.3.4	Thermodynamically Stable and Metastable Solid Solutions	104
2.3.5	Experimental Methods for Studying Solid Solutions	104
2.3.5.1	X-ray Powder Diffraction, XRD	104
2.3.5.2	Density Measurements	105
2.3.5.3	Changes in Other Properties – Thermal Activity and DTA/DSC	107
2.4	Extended Defects	108
2.4.1	Crystallographic Shear Structures	108
2.4.2	Stacking Faults	110
2.4.3	Subgrain Boundaries and Antiphase Domains (Boundaries)	110
2.5	Dislocations and Mechanical Properties of Solids	111
2.5.1	Edge Dislocations	112
2.5.2	Screw Dislocations	114
2.5.3	Dislocation Loops	115
2.5.4	Dislocations and Crystal Structure	117
2.5.5	Mechanical Properties of Metals	118
2.5.6	Dislocations, Vacancies and Stacking Faults	120
2.5.7	Dislocations and Grain Boundaries	122
3	Bonding in Solids	125
3.1	Overview: Ionic, Covalent, Metallic, van der Waals and Hydrogen Bonding in Solids	125
3.2	Ionic Bonding	126
3.2.1	Ions and Ionic Radii	126
3.2.2	Ionic Structures – General Principles	130
3.2.3	The Radius Ratio Rules	133
3.2.4	Borderline Radius Ratios and Distorted Structures	135
3.2.5	Lattice Energy of Ionic Crystals	136
3.2.6	Kapustinskii’s Equation	140
3.2.7	The Born–Haber Cycle and Thermochemical Calculations	141
3.2.8	Stabilities of Real and Hypothetical Ionic Compounds	143
3.2.8.1	Inert Gas Compounds	143
3.2.8.2	Lower and Higher Valence Compounds	144
3.2.9	Effect of Partial Covalent Bonding on Crystal Structures	145
3.2.10	Effective Nuclear Charge	147
3.2.11	Electronegativity and Partially Charged Atoms	147
3.2.12	Coordinated Polymeric Structures – Sanderson’s Model	149
3.2.13	Mooser–Pearson Plots and Ionicities	150

3.2.14	Bond Valence and Bond Length	151
3.2.15	Non-Bonding Electron Effects	153
	3.2.15.1 d-Electron Effects	153
	3.2.15.2 Inert Pair Effect	161
3.3	Covalent Bonding	161
3.3.1	Particle-Wave Duality, Atomic Orbitals, Wavefunctions and Nodes	162
3.3.2	Orbital Overlap, Symmetry and Molecular Orbitals	163
3.3.3	Valence Bond Theory, Electron Pair Repulsion, Hybridisation and Oxidation States	169
3.4	Metallic Bonding and Band Theory	173
3.4.1	Band Structure of Metals	179
3.4.2	Band Structure of Insulators	179
3.4.3	Band Structure of Semiconductors: Silicon	179
3.4.4	Band Structure of Inorganic Solids	181
	3.4.4.1 III–V, II–VI and I–VII Compounds	181
	3.4.4.2 Transition Metal Compounds	182
	3.4.4.3 Fullerenes and Graphite	184
3.5	Bands or Bonds: a Final Comment	185
4	Synthesis, Processing and Fabrication Methods	187
4.1	General Observations	187
4.2	Solid State Reaction or Shake 'n Bake Methods	187
4.2.1	Nucleation and Growth, Epitaxy and Topotaxy	188
4.2.2	Practical Considerations and Some Examples of Solid State Reactions	191
	4.2.2.1 Li_4SiO_4	193
	4.2.2.2 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	193
	4.2.2.3 Na β/β'' alumina	193
4.2.3	Combustion Synthesis	194
4.2.4	Mechanosynthesis	195
4.3	Low Temperature or Chimie Douce Methods	196
4.3.1	Alkoxide Sol–Gel Method	196
	4.3.1.1 Synthesis of MgAl_2O_4	197
	4.3.1.2 Synthesis of Silica Glass	197
	4.3.1.3 Spinning of Alumina Fibres	197
	4.3.1.4 Preparation of Indium Tin Oxide (ITO) and Other Coatings	198
	4.3.1.5 Fabrication of YSZ Ceramics	198
4.3.2	Sol–Gel Method Using Oxyhydroxides and Colloid Chemistry	198
	4.3.2.1 Synthesis of Zeolites	199
	4.3.2.2 Preparation of Alumina-Based Abrasives and Films	200
4.3.3	Citrate Gel and Pechini Processes	200
4.3.4	Use of Homogeneous, Single-Source Precursors	201
4.3.5	Hydrothermal and Solvothermal Synthesis	202
4.3.6	Microwave Synthesis	204
4.3.7	Intercalation and Deintercalation	205
	4.3.7.1 Graphite Intercalation Compounds	207
	4.3.7.2 Pillared Clays and Layered Double Hydroxides	208
	4.3.7.3 Synthesis of Graphene	209

4.3.8	Example of a Difficult Synthesis Made Possible by Chimie Douce Methods: BiFeO ₃	211
4.3.9	Molten Salt Synthesis, MSS	212
4.4	Gas-Phase Methods	213
4.4.1	Vapour-Phase Transport	213
4.4.2	Chemical Vapour Deposition, CVD	216
4.4.2.1	Amorphous Silicon	217
4.4.2.2	Diamond Films	219
4.4.3	Sputtering and Evaporation	221
4.4.4	Atomic Layer Deposition, ALD	222
4.4.5	Aerosol Synthesis and Spray Pyrolysis	223
4.5	High-Pressure Methods	225
4.6	Crystal Growth	226
4.6.1	Czochralski Method	226
4.6.2	Bridgman and Stockbarger Methods	226
4.6.3	Zone Melting	227
4.6.4	Precipitation from Solution or Melt: Flux Method	227
4.6.5	Verneuil Flame Fusion Method	228
5	Crystallography and Diffraction Techniques	229
5.1	General Comments: Molecular and Non-Molecular Solids	229
5.1.1	Identification of Crystalline Solids	229
5.1.2	Structure of Non-Molecular Crystalline Solids	229
5.1.3	Defects, Impurities and Stoichiometry of Crystalline Solids	230
5.2	Characterisation of Solids	231
5.3	X-Ray Diffraction	232
5.3.1	Generation of X-Rays	232
5.3.1.1	Laboratory Sources Utilising Inner Shell Electronic Transitions	232
5.3.1.2	Synchrotron X-ray Sources	235
5.3.2	Interaction of X-Rays with Matter	235
5.3.3	Optical Grating and Diffraction of Light	236
5.3.4	Crystals and Diffraction of X-Rays	238
5.3.4.1	The Laue Equations	238
5.3.4.2	Bragg's Law	239
5.3.5	X-Ray Diffraction Methods	240
5.3.6	The Powder Method – Principles and Uses	240
5.3.6.1	Focusing of X-rays: Theorem of a Circle	243
5.3.6.2	Crystal Monochromators	244
5.3.6.3	Powder Diffractometers	244
5.3.6.4	Guinier Focusing Cameras	245
5.3.6.5	A Powder Pattern of a Crystalline Phase is its 'Fingerprint'	246
5.3.6.6	Powder Patterns and Crystal Structures	247
5.3.7	Intensities	248
5.3.7.1	Scattering of X-rays by an Atom: Atomic Scattering Factors or Form Factors	249
5.3.7.2	Scattering of X-rays by a Crystal – Systematic Absences	250
5.3.7.3	General Equation for Phase Difference, δ	253

	5.3.7.4	Intensities and Structure Factors	255
	5.3.7.5	Temperature Factors	258
	5.3.7.6	R-Factors and Structure Determination	259
	5.3.7.7	Structure Refinement from Powder Data: Rietveld Refinement	259
5.3.8		X-Ray Crystallography and Structure Determination – What is Involved?	260
	5.3.8.1	The Patterson Method	263
	5.3.8.2	Fourier Methods	264
	5.3.8.3	Direct Methods	264
	5.3.8.4	Electron Density Maps	265
5.4		Electron Diffraction	265
5.5		Neutron Diffraction	266
	5.5.1	Crystal Structure Determination	267
	5.5.2	Magnetic Structure Analysis	268
	5.5.3	Inelastic Scattering, Soft Modes and Phase Transitions	269
6		Other Techniques: Microscopy, Spectroscopy, Thermal Analysis	271
6.1		Diffraction and Microscopic Techniques: What Do They Have in Common?	271
6.2		Optical and Electron Microscopy Techniques	272
	6.2.1	Optical Microscopy	272
	6.2.1.1	Polarising Microscope	273
	6.2.1.2	Reflected Light Microscope	276
	6.2.2	Electron Microscopy	276
	6.2.2.1	Scanning Electron Microscopy	280
	6.2.2.2	Electron Probe Microanalysis, EPMA, and Energy-Dispersive X-ray Spectroscopy, EDS or EDX	281
	6.2.2.3	Auger Electron (Emission) Microscopy and Spectroscopy, AES	282
	6.2.2.4	Cathodoluminescence, CL	284
	6.2.2.5	Transmission Electron Microscopy, TEM, and Scanning Transmission Electron Microscopy, STEM	287
	6.2.2.6	Electron Energy Loss Spectroscopy, EELS	288
	6.2.2.7	High-Angle Annular Dark Field, HAADF/Z-Contrast STEM	289
6.3		Spectroscopic Techniques	291
	6.3.1	Vibrational Spectroscopy: IR and Raman	293
	6.3.2	Visible and Ultraviolet (UV) Spectroscopy	296
	6.3.3	Nuclear Magnetic Resonance (NMR) Spectroscopy	298
	6.3.4	Electron Spin Resonance (ESR) Spectroscopy	301
	6.3.5	X-Ray Spectroscopies: XRF, AEFS, EXAFS	303
	6.3.5.1	Emission Techniques	303
	6.3.5.2	Absorption Techniques	305
	6.3.6	Electron Spectroscopies: ESCA, XPS, UPS, AES, EELS	308
	6.3.7	Mössbauer Spectroscopy	312
6.4		Thermal Analysis (TA)	314
	6.4.1	Thermogravimetry (TG)	315
	6.4.2	Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)	315
	6.4.3	Applications	317
6.5		Strategy to Identify, Analyse and Characterise ‘Unknown’ Solids	321

7	Phase Diagrams and their Interpretation	325
7.1	The Phase Rule, the Condensed Phase Rule and Some Definitions	325
7.2	One-Component Systems	330
7.2.1	The System H_2O	331
7.2.2	The System SiO_2	332
7.2.3	Condensed One-Component Systems	333
7.3	Two-Component Condensed Systems	333
7.3.1	A Simple Eutectic System	333
7.3.1.1	Liquidus and Solidus	335
7.3.1.2	Eutectic	335
7.3.1.3	Lever Rule	335
7.3.1.4	Eutectic Reaction	336
7.3.1.5	The Liquidus, Saturation Solubilities and Freezing Point Depression	337
7.3.2	Binary Systems with Compounds	337
7.3.2.1	Congruent Melting	337
7.3.2.2	Incongruent Melting, Peritectic Point, Peritectic Reaction	337
7.3.2.3	Non-Equilibrium Effects	339
7.3.2.4	Upper and Lower Limits of Stability	340
7.3.3	Binary Systems with Solid Solutions	340
7.3.3.1	Complete Solid Solution	340
7.3.3.2	Fractional Crystallisation	341
7.3.3.3	Thermal Maxima and Minima	342
7.3.3.4	Partial Solid Solution Systems	342
7.3.4	Binary Systems with Solid–Solid Phase Transitions	344
7.3.5	Binary Systems with Phase Transitions and Solid Solutions: Eutectoids and Peritectoids	345
7.3.6	Binary Systems with Liquid Immiscibility: MgO – SiO_2	347
7.3.7	Some Technologically Important Phase Diagrams	348
7.3.7.1	The System Fe – C : Iron and Steel Making	348
7.3.7.2	The System CaO – SiO_2 : Cement Manufacture	349
7.3.7.3	The System Na – S : Na/S Batteries	350
7.3.7.4	The System Na_2O – SiO_2 : Glass Making	351
7.3.7.5	The System Li_2O – SiO_2 : Metastable Phase Separation and Synthetic Opals	352
7.3.7.6	Purification of Semiconducting Si by Zone Refining	353
7.3.7.7	The System ZrO_2 – Y_2O_3 : Ytria-Stabilised Zirconia, YSZ, Solid Electrolyte	354
7.3.7.8	The System Bi_2O_3 – Fe_2O_3 : Multiferroic BiFeO_3	354
7.4	Some Tips and Guidelines for Constructing Binary Phase Diagrams	355
8	Electrical Properties	359
8.1	Survey of Electrical Properties and Electrical Materials	359
8.2	Metallic Conductivity	361
8.2.1	Organic Metals: Conjugated Systems	362
8.2.1.1	Polyacetylene	362
8.2.1.2	Poly- <i>p</i> -Phenylene and Polypyrrole	364
8.2.2	Organic Metals: Charge-Transfer Complexes	365

8.3	Superconductivity	366
8.3.1	The Property of Zero Resistance	366
8.3.2	Perfect Diamagnetism; the Meissner Effect	368
8.3.3	Critical Temperature T_c , Critical Field H_c and Critical Current J_c	368
8.3.4	Type I and Type II Superconductors: The Vortex (Mixed) State	370
8.3.5	Survey of Superconducting Materials	371
8.3.6	Crystal Chemistry of Cuprate Perovskites	374
8.3.7	YBa ₂ Cu ₃ O _{7-δ} , YBCO	376
8.3.7.1	Crystal Structure	376
8.3.7.2	Atom Valences and the Superconducting Mechanism	378
8.3.7.3	Oxygen Content of YBa ₂ Cu ₃ O _{7-δ}	378
8.3.7.4	Determination of Oxygen Content, 7- δ	380
8.3.8	Fullerides	381
8.3.9	Applications of Superconductors	381
8.4	Semiconductivity	382
8.4.1	Elemental and Compound Semiconductors with Diamond and Zinc Blende Structures	384
8.4.2	Electrical Properties of Semiconductors	386
8.4.3	Oxide Semiconductors	388
8.4.4	Applications of Semiconductors	389
8.5	Ionic Conductivity	392
8.5.1	Alkali Halides: Vacancy Conduction	393
8.5.1.1	Activation Energy for Ion Hopping: Geometric Considerations	394
8.5.1.2	Ionic Conductivity of NaCl Crystals	396
8.5.1.3	Extrinsic Conductivity in NaCl: Control by Aliovalent Doping	397
8.5.2	Silver Chloride: Interstitial Conduction	399
8.5.3	Alkaline Earth Fluorides	401
8.5.4	Solid Electrolytes (or Fast Ion Conductors, Superionic Conductors)	401
8.5.4.1	General Considerations	401
8.5.4.2	β -Alumina	403
8.5.4.3	Nasicon	409
8.5.4.4	Hollandites and Priderites	409
8.5.4.5	Silver and Copper Ion Conductors	411
8.5.4.6	Fluoride Ion Conductors	413
8.5.4.7	Oxide Ion Conductors	414
8.5.4.8	Li ⁺ Ion Conductors	418
8.5.4.9	Proton Conductors	421
8.5.4.10	Mixed Ionic/Electronic Conductors	421
8.5.4.11	Applications of Solid Electrolytes and Mixed Conductors	422
8.6	Dielectric Materials	430
8.6.1	From Dielectrics to Conductors	433
8.7	Ferroelectrics	436
8.8	Pyroelectrics	441
8.9	Piezoelectrics	441
8.10	Applications of Ferro-, Pyro- and Piezoelectrics	441

9	Magnetic Properties	445
9.1	Physical Properties	445
9.1.1	Behaviour of Substances in a Magnetic Field	446
9.1.2	Effects of Temperature: Curie and Curie–Weiss Laws	448
9.1.3	Magnetic Moments	449
9.1.4	Mechanisms of Ferro- and Antiferromagnetic Ordering: Superexchange	452
9.1.5	Some More Definitions	453
9.2	Magnetic Materials, their Structures and Properties	455
9.2.1	Metals and Alloys	455
9.2.2	Transition Metal Monoxides	458
9.2.3	Transition Metal Dioxides	459
9.2.4	Spinels	459
9.2.5	Garnets	462
9.2.6	Ilmenites and Perovskites	464
9.2.7	Magnetoplumbites	464
9.3	Applications: Structure–Property Relations	464
9.3.1	Transformer Cores	464
9.3.2	Permanent Magnets	466
9.3.3	Magnetic Information Storage	466
9.4	Recent Developments	467
9.4.1	Magnetoresistance: Giant and Colossal	467
9.4.2	Multiferroics	469
10	Optical Properties: Luminescence and Lasers	473
10.1	Visible Light and the Electromagnetic Spectrum	473
10.2	Sources of Light, Thermal Sources, Black Body Radiation and Electronic Transitions	473
10.3	Scattering Processes: Reflection, Diffraction and Interference	476
10.4	Luminescence and Phosphors	476
10.5	Configurational Coordinate Model	478
10.6	Some Phosphor Materials	480
10.7	Anti-Stokes Phosphors	481
10.8	Stimulated Emission, Amplification of Light and Lasers	482
10.8.1	The Ruby Laser	484
10.8.2	Neodymium Lasers	485
10.8.3	Semiconductor Lasers and the Light-Emitting Diode, LED	486
10.9	Photodetectors	488
10.10	Fibre-Optics	490
10.11	Solar Cells	492
	Further Reading	493
	Appendix A: Interplanar Spacings and Unit Cell Volumes	505
	Appendix B: Model Building	507
	Appendix C: Geometrical Considerations in Crystal Chemistry	511

Appendix D: How to Recognise Close Packed (Eutactic) Structures	515
Appendix E: Positive and Negative Atomic Coordinates	517
Appendix F: The Elements and Some of Their Properties	519
Questions	525
Index	537