

# **Solid State Chemistry and its Applications**

**Second Edition**

**ANTHONY R. WEST**

*Department of Materials Science and Engineering,  
University of Sheffield, UK*

**WILEY**

# Contents

Preface	xxi
Companion Website	xxiii
Biography	xxv
Solid State Chemistry, an Overview of the Discipline: Chemistry – Solid State Chemistry – Materials Chemistry – Materials Science and Engineering	1
1    Crystal Structures, Crystal Chemistry, Symmetry and Space Groups	7
1.1    Unit Cells and Crystal Systems	7
1.2    Symmetry	9
1.2.1    Rotational symmetry; symmetry elements and operations	9
1.2.2    Quasicrystals	12
1.2.3    Mirror symmetry	14
1.2.4    Centre of symmetry and inversion axes	14
1.2.5    Point symmetry and space symmetry	15
1.3    Symmetry and Choice of Unit Cell	16
1.4    Lattice, Bravais Lattice	18
1.5    Lattice Planes and Miller Indices	20
1.6    Indices of Directions	22
1.7 $d$ -Spacing Formulae	23
1.8    Crystal Densities and Unit Cell Contents	23
1.9    Description of Crystal Structures	24
1.10    Close Packed Structures – Cubic and Hexagonal Close Packing	25
1.11    Relationship Between Cubic Close Packed and Face Centred Cubic	27
1.12    Hexagonal Unit Cell and Close Packing	27
1.13    Density of Close Packed Structures	28
1.14    Unit Cell Projections and Atomic Coordinates	30
1.15    Materials that can be Described as Close Packed	31
1.15.1    Metals	31
1.15.2    Alloys	31
1.15.3    Ionic structures	32
1.15.3.1    Tetrahedral and octahedral sites	33
1.15.3.2    Relative sizes of tetrahedral and octahedral sites	35

1.15.3.3	Location of tetrahedral and octahedral sites in an <i>fcc</i> unit cell; bond length calculations	35
1.15.3.4	Description of crystal structures; fractional atomic coordinates	36
1.15.4	Covalent network structures	37
1.15.5	Molecular structures	37
1.15.6	Fullerenes and fullerides	38
1.16	Structures Built of Space-Filling Polyhedra	39
1.17	Some Important Structure Types	42
1.17.1	Rock salt ( $\text{NaCl}$ ), zinc blende or sphalerite ( $\text{ZnS}$ ), fluorite ( $\text{CaF}_2$ ), antifluorite ( $\text{Na}_2\text{O}$ )	42
1.17.1.1	Rock salt structure	44
1.17.1.2	Zinc blende (sphalerite) structure	45
1.17.1.3	Antifluorite/fluorite structure	46
1.17.1.4	Cuprite structure, $\text{Cu}_2\text{O}$	48
1.17.1.5	Bond length calculations	48
1.17.2	Diamond	48
1.17.3	Wurtzite ( $\text{ZnS}$ ) and nickel arsenide ( $\text{NiAs}$ )	49
1.17.4	Caesium chloride ( $\text{CsCl}$ )	54
1.17.5	Other AX structures	55
1.17.6	Rutile ( $\text{TiO}_2$ ), cadmium iodide ( $\text{CdI}_2$ ), cadmium chloride ( $\text{CdCl}_2$ ) and caesium oxide ( $\text{Cs}_2\text{O}$ )	55
1.17.7	Perovskite	61
1.17.7.1	Tolerance factor	63
1.17.7.2	$\text{BaTiO}_3$	64
1.17.7.3	Tilted perovskites: Glazer notation	64
1.17.7.4	$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , CCTO	65
1.17.7.5	Anion-deficient perovskites	70
1.17.7.6	Stoichiometry–property relations	71
1.17.7.7	Cation-ordered perovskites	71
1.17.7.8	Hybrid organic–inorganic halide perovskites	73
1.17.7.9	Anti-perovskites	74
1.17.7.10	Mixed anion perovskites: oxynitrides and oxyfluorides	74
1.17.7.11	Hexagonal perovskites	74
1.17.8	Rhenium trioxide ( $\text{ReO}_3$ ), perovskite tungsten bronzes, tetragonal tungsten bronzes and tunnel structures	76
1.17.9	Spinel	79
1.17.10	Olivine	83
1.17.11	Corundum, ilmenite and $\text{LiNbO}_3$	85
1.17.12	Fluorite-related structures, pyrochlore, weberite and rare earth sesquioxides	85
1.17.13	Garnet	90
1.17.14	Perovskite–rock salt intergrowth structures: $\text{K}_2\text{NiF}_4$ , Ruddlesden–Popper, Aurivillius and Dion Jacobsen phases and layered cuprate superconductors	91
1.17.15	The aluminium diboride structure ( $\text{AlB}_2$ )	95
1.17.16	Silicate structures – some tips to understanding them	96
18	Point Groups and Space Groups	99
1.18.1	Point groups	99
1.18.2	Stereographic projections and equivalent positions	100
1.18.3	Point symmetry of molecules: general and special positions	105

1.18.4	Centrosymmetric and non-centrosymmetric point groups	106
1.18.5	Space groups	107
1.18.5.1	Triclinic $P\bar{1}$	107
1.18.5.2	Monoclinic C2	109
1.18.5.3	Monoclinic $C2/m$	111
1.18.5.4	Orthorhombic $P222_1$	113
1.18.5.5	Orthorhombic F222	113
1.18.5.6	Tetragonal $I4_1$	114
1.18.6	Space groups and crystal structures	115
1.18.6.1	The perovskite structure, $SrTiO_3$	115
1.18.6.2	The rutile structure, $TiO_2$	116
1.18.7	Systematic absences in diffraction patterns and space groups	117
<b>2</b>	<b>Crystal Defects, Non-stoichiometry and Solid Solutions</b>	<b>119</b>
2.1	Perfect and Imperfect Crystals	119
2.2	Types of Defect: Point Defects	120
2.2.1	Schottky defect	121
2.2.2	Frenkel defect	121
2.2.2.1	The Kroger–Vink notation for crystal defects	122
2.2.2.2	Thermodynamics of Schottky and Frenkel defect formation	122
2.2.3	Colour centres	126
2.2.4	Vacancies and interstitials in non-stoichiometric crystals: extrinsic and intrinsic defects	127
2.2.5	Defect clusters or aggregates	128
2.2.6	Interchanged atoms: order-disorder phenomena	131
2.3	Solid Solutions of Ionic Materials	131
2.3.1	Substitutional solid solutions	132
2.3.2	Interstitial solid solutions	134
2.3.3	More complex solid solution mechanisms: aliovalent substitution	135
2.3.3.1	Ionic compensation mechanisms	135
2.3.3.2	Electronic compensation: metals, semi- and superconductors	138
2.3.4	Thermodynamically stable and metastable solid solutions	140
2.3.5	Experimental methods for studying solid solutions	140
2.3.5.1	X-ray powder diffraction, XRD	140
2.3.5.2	Density measurements	141
2.3.5.3	Changes in other properties – thermal activity and DTA/DSC	142
2.4	Extended Defects	143
2.4.1	Crystallographic shear structures	143
2.4.2	Stacking faults	145
2.4.3	Subgrain boundaries and antiphase domains (boundaries)	146
2.4.4	When do defects in a structure become a new structure?	147
2.5	Dislocations and Mechanical Properties of Solids	147
2.5.1	Edge dislocations	148
2.5.2	Screw dislocations	150
2.5.3	Dislocation loops	151
2.5.4	Dislocations and crystal structure	152
2.5.5	Mechanical properties of metals	153
2.5.6	Dislocations, vacancies and stacking faults	156
2.5.7	Dislocations and grain boundaries	158

<b>3 Bonding in Solids</b>	<b>161</b>
3.1 Overview: Ionic, Covalent, Metallic, van der Waals and Hydrogen Bonding in Solids	161
3.2 Ionic Bonding	162
3.2.1 Ions and ionic radii	162
3.2.2 Ionic structures – general principles	166
3.2.3 The radius ratio rules	168
3.2.4 Borderline radius ratios and distorted structures	171
3.2.5 Lattice energy of ionic crystals	172
3.2.6 Kapustinskii's equation	175
3.2.7 The Born–Haber cycle and thermochemical calculations	176
3.2.8 Stabilities of real and hypothetical ionic compounds	178
3.2.8.1 Inert gas compounds	178
3.2.8.2 Lower and higher valence compounds	179
3.2.9 Effect of partial covalent bonding on crystal structures	181
3.2.10 Effective nuclear charge	182
3.2.11 Electronegativity and partially charged atoms	183
3.2.12 Coordinated polymeric structures – Sanderson's model	184
3.2.13 Mooser–Pearson plots and ionicities	185
3.2.14 Bond valence and bond length	186
3.2.15 Non-bonding electron effects	188
3.2.15.1 <i>d</i> -Electron effects	188
3.2.15.2 Inert pair effect	196
3.3 Covalent Bonding	196
3.3.1 Particle-wave duality, atomic orbitals, wavefunctions and nodes	197
3.3.2 Orbital overlap, symmetry and molecular orbitals	198
3.3.3 Valence bond theory, electron pair repulsion, hybridisation and oxidation states	204
3.4 Metallic Bonding and Band Theory	207
3.4.1 Band structure of metals	213
3.4.2 Band structure of insulators	214
3.4.3 Band structure of semiconductors: silicon	214
3.4.4 Band structure of inorganic solids	215
3.4.4.1 III–V, II–VI and I–VII compounds	215
3.4.4.2 Transition metal compounds	216
3.4.4.3 Fullerenes and graphite	218
3.5 Bands or Bonds: A Final Comment	220
<b>4 Synthesis, Processing and Fabrication Methods</b>	<b>221</b>
4.1 General Observations	221
4.2 Solid State Reaction or Shake 'n Bake Methods	221
4.2.1 Nucleation and growth, epitaxy and topotaxy	222
4.2.2 Practical considerations and some examples of solid state reactions	225
4.2.2.1 $\text{Li}_4\text{SiO}_4$	226
4.2.2.2 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	227
4.2.2.3 $\text{Na } \beta/\beta''$ alumina	227
4.2.3 Combustion synthesis	228
4.2.4 Mechanochemical synthesis	229

<b>4.3 Low Temperature or Chimie Douce Methods</b>	<b>230</b>
<b>4.3.1 Alkoxide sol-gel method</b>	<b>230</b>
4.3.1.1 Synthesis of MgAl <sub>2</sub> O <sub>4</sub>	231
4.3.1.2 Synthesis of silica glass	231
4.3.1.3 Spinning of alumina fibres	231
4.3.1.4 Preparation of indium tin oxide (ITO) and other coatings	232
4.3.1.5 Fabrication of YSZ ceramics	232
<b>4.3.2 Sol-gel method using oxyhydroxides; solution chemistry of Al and Fe</b>	<b>232</b>
4.3.2.1 Synthesis of zeolites	234
4.3.2.2 Preparation of alumina-based abrasives and films	234
<b>4.3.3 Citrate gel and Pechini processes</b>	<b>235</b>
<b>4.3.4 Use of homogeneous, single-source precursors</b>	<b>236</b>
<b>4.3.5 Hydrothermal and solvothermal synthesis</b>	<b>237</b>
<b>4.3.6 Microwave synthesis</b>	<b>238</b>
<b>4.3.7 Intercalation and deintercalation</b>	<b>240</b>
4.3.7.1 Graphite intercalation compounds	241
4.3.7.2 Pillared clays and layered double hydroxides	242
4.3.7.3 Synthesis of graphene	243
<b>4.3.8 Example of a difficult synthesis made possible by chimie douce methods: BiFeO<sub>3</sub></b>	<b>245</b>
<b>4.3.9 Molten salt synthesis, MSS</b>	<b>246</b>
<b>4.4 Gas-Phase Methods</b>	<b>247</b>
<b>4.4.1 Vapour-phase transport</b>	<b>247</b>
<b>4.4.2 Chemical vapour deposition, CVD</b>	<b>250</b>
4.4.2.1 Amorphous silicon	251
4.4.2.2 Diamond films	253
<b>4.4.3 Sputtering and evaporation, pulsed laser deposition, PLD and molecular beam epitaxy, MBE</b>	<b>255</b>
<b>4.4.4 Atomic layer deposition, ALD</b>	<b>257</b>
<b>4.4.5 Aerosol synthesis and spray pyrolysis</b>	<b>257</b>
<b>4.5 High-Pressure Methods</b>	<b>258</b>
<b>4.6 Crystal Growth</b>	<b>261</b>
<b>4.6.1 Czochralski method</b>	<b>261</b>
<b>4.6.2 Bridgman and Stockbarger methods</b>	<b>261</b>
<b>4.6.3 Zone melting</b>	<b>262</b>
<b>4.6.4 Precipitation from solution or melt: flux method</b>	<b>262</b>
<b>4.6.5 Verneuil flame fusion method</b>	<b>262</b>
<b>4.6.6 Skull melting</b>	<b>263</b>
<b>5 Crystallography and Diffraction Techniques</b>	<b>265</b>
<b>5.1 General Comments: Molecular and Non-Molecular Solids</b>	<b>265</b>
<b>5.1.1 Identification of crystalline solids</b>	<b>265</b>
<b>5.1.2 Structure of non-molecular crystalline solids</b>	<b>265</b>
<b>5.1.3 Defects, impurities and stoichiometry of crystalline solids</b>	<b>266</b>
<b>5.2 Characterisation of Solids</b>	<b>267</b>
<b>5.3 X-Ray Diffraction</b>	<b>268</b>
<b>5.3.1 Generation of X-rays</b>	<b>268</b>
5.3.1.1 Laboratory sources utilising inner shell electronic transitions	268
5.3.1.2 Synchrotron X-ray sources	271

5.3.2	Interaction of X-rays with matter	271
5.3.3	Optical grating and diffraction of light	272
5.3.4	Crystals and diffraction of X-rays	274
5.3.4.1	The Laue equations	274
5.3.4.2	Bragg's law	275
5.3.5	X-ray diffraction methods	276
5.3.6	The powder method – principles and uses	276
5.3.6.1	Focusing of X-rays: theorem of a circle	279
5.3.6.2	Crystal monochromators	279
5.3.6.3	Powder diffractometers	280
5.3.6.4	Guinier focusing cameras	281
5.3.6.5	A powder pattern of a crystalline phase is its 'fingerprint'	281
5.3.6.6	Powder patterns and crystal structures	283
5.3.6.7	Powder patterns from single crystals: the Gandolfi technique	284
5.3.7	Intensities	285
5.3.7.1	Scattering of X-rays by an atom: atomic scattering factors or form factors	285
5.3.7.2	Scattering of X-rays by a crystal – systematic absences	287
5.3.7.3	General equation for phase difference, $\delta$	289
5.3.7.4	Intensities and structure factors	291
5.3.7.5	Temperature factors	294
5.3.7.6	R-factors and structure determination	295
5.3.7.7	Structure refinement from powder data: Rietveld refinement	295
5.3.8	X-ray crystallography and structure determination - what is involved?	296
5.3.8.1	The Patterson method	299
5.3.8.2	Fourier methods	300
5.3.8.3	Direct methods	300
5.3.8.4	Electron density maps	301
5.4	Electron Diffraction	301
5.5	Neutron Diffraction	302
5.5.1	Crystal structure determination	303
5.5.2	Magnetic structure analysis	304
5.5.3	Inelastic scattering, soft modes and phase transitions	305
5.6	The Reciprocal Lattice	306
5.6.1	Real and reciprocal lattices	306
5.6.2	Direct observation of the reciprocal lattice and systematic absences (extinctions)	310
5.6.3	Diffraction and the reciprocal lattice: the Ewald sphere of reflection	314
5.6.4	Selected area electron diffraction	317
5.7	Total scattering and pair distribution function (PDF) analysis	319
5.8	Line broadening of XRD powder patterns, domain (particle) size measurement and strain effects	322
<b>6</b>	<b>Other Characterisation Techniques: Microscopy, Spectroscopy, Thermal Analysis</b>	<b>325</b>
6.1	Diffraction and Microscopic Techniques: What Do They Have in Common?	325
6.2	Optical and Electron Microscopy Techniques	326
6.2.1	Optical microscopy	326
6.2.1.1	Polarising microscope	327
6.2.1.2	Reflected light microscope	330
6.2.2	Electron microscopy	330

6.2.2.1	Scanning electron microscopy	334
6.2.2.2	Electron probe microanalysis, EPMA, and energy-dispersive X-ray spectroscopy, EDS or EDX	336
6.2.2.3	Auger electron (emission) microscopy and spectroscopy, AES	336
6.2.2.4	Cathodoluminescence, CL	339
6.2.2.5	Transmission electron microscopy, TEM, and scanning transmission electron microscopy, STEM	341
6.2.2.6	Electron energy loss spectroscopy, EELS	342
6.2.2.7	High-angle annular dark field, HAADF/Z-contrast STEM	343
<b>6.3</b>	<b>Spectroscopic Techniques</b>	<b>345</b>
6.3.1	Vibrational spectroscopy: IR and Raman	346
6.3.2	Visible and ultraviolet (UV) spectroscopy	350
6.3.3	Nuclear magnetic resonance (NMR) spectroscopy	352
6.3.4	Electron spin resonance (ESR) spectroscopy	356
6.3.5	X-ray spectroscopies: XRF, AEFS, EXAFS	358
6.3.5.1	Emission techniques	358
6.3.5.2	Absorption techniques	360
6.3.6	Electron spectroscopies: ESCA, XPS, UPS, AES, EELS	363
6.3.7	Mössbauer spectroscopy	367
<b>6.4</b>	<b>Thermal Analysis (TA)</b>	<b>370</b>
6.4.1	Thermogravimetry (TG)	370
6.4.2	Differential thermal analysis (DTA) and differential scanning calorimetry (DSC)	371
6.4.3	Applications	372
<b>6.5</b>	<b>Strategy to Identify, Analyse and Characterise ‘Unknown’ Solids</b>	<b>376</b>
<b>7</b>	<b>Phase Diagrams and Their Interpretation</b>	<b>381</b>
7.1	The Phase Rule, the Condensed Phase Rule and Some Definitions	381
7.2	One-Component Systems	386
7.2.1	The system $H_2O$	387
7.2.2	The system $SiO_2$	387
7.2.3	Condensed one-component systems	388
<b>7.3</b>	<b>Two-Component Condensed Systems</b>	<b>389</b>
7.3.1	A simple eutectic system	389
7.3.1.1	Liquidus and solidus	390
7.3.1.2	Eutectic	391
7.3.1.3	Lever rule	391
7.3.1.4	Eutectic reaction	392
7.3.1.5	The liquidus, saturation solubilities and freezing point depression	392
7.3.2	Binary systems with compounds	393
7.3.2.1	Congruent melting	393
7.3.2.2	Incongruent melting, peritectic point, peritectic reaction	394
7.3.2.3	Non-equilibrium effects	394
7.3.2.4	Upper and lower limits of stability	395
7.3.3	Binary systems with solid solutions	395
7.3.3.1	Complete solid solution	395
7.3.3.2	Fractional crystallisation	396
7.3.3.3	Thermal maxima and minima	397
7.3.3.4	Partial solid solution systems	397

7.3.4	Binary systems with solid–solid phase transitions	400
7.3.5	Binary systems with phase transitions and solid solutions: eutectoids and peritectoids	400
7.3.6	Binary systems with liquid immiscibility: MgO–SiO <sub>2</sub>	402
7.3.7	Some technologically important phase diagrams	404
7.3.7.1	The system Fe–C: iron and steel making	404
7.3.7.2	The system CaO–SiO <sub>2</sub> : cement manufacture	405
7.3.7.3	The system Na–S: Na/S batteries	405
7.3.7.4	The system Na <sub>2</sub> O–SiO <sub>2</sub> : glass making	407
7.3.7.5	The system Li <sub>2</sub> O–SiO <sub>2</sub> : metastable phase separation and synthetic opals	408
7.3.7.6	Purification of semiconducting Si by zone refining	409
7.3.7.7	The system ZrO <sub>2</sub> –Y <sub>2</sub> O <sub>3</sub> : yttria-stabilised zirconia, YSZ, solid electrolyte	409
7.3.7.8	The system Bi <sub>2</sub> O <sub>3</sub> –Fe <sub>2</sub> O <sub>3</sub> : multiferroic BiFeO <sub>3</sub>	410
7.4	Some Tips and Guidelines for Constructing Binary Phase Diagrams	411
7.5	Ternary Systems	413
7.5.1	Subsolidus equilibria	415
7.5.2	Subsolidus equilibria with solid solutions	416
7.5.3	Solid–liquid phase diagrams	421
7.5.3.1	Simple ternary eutectic system	421
7.5.3.2	Ternary systems containing binary compounds	424
7.5.3.3	Ternary systems containing solid solutions	430
7.5.3.4	Analogy between ternary phase diagrams, crystallisation pathways, geographical contour maps and hill walking	431
7.5.3.5	Some important ternary phase diagrams	433
7.6	Phase Transitions	439
7.6.1	What is a phase transition?	439
7.6.2	Buerger's classification: reconstructive and displacive transitions	440
7.6.3	Thermodynamic classification of phase transitions	444
7.6.4	Applications of G–T diagrams; stable and metastable phases	450
7.6.5	Representation of phase transitions on phase diagrams	453
7.6.6	Kinetics of phase transitions	453
7.6.7	Critical size of nuclei	455
7.6.8	Rate equations	457
7.6.8.1	Nucleation rate	457
7.6.8.2	Overall transformation rate; the Avrami equation	458
7.6.8.3	Time–temperature–transformation (TTT) diagrams	459
7.6.9	Kinetics of phase transitions and solid state reactions	459
7.6.10	Crystal chemistry and phase transitions	462
7.6.10.1	Structural changes with increasing temperature and pressure	462
7.6.10.2	Martensitic transformations	464
7.6.10.3	Order–disorder transitions	466
<b>8</b>	<b>Electrical Properties</b>	<b>469</b>
8.1	Survey of Electrical Properties and Electrical Materials	469
8.2	Metallic Conductivity	471
8.2.1	Organic metals: conjugated systems	472

8.2.1.1	Polyacetylene	472
8.2.1.2	Poly- <i>p</i> -phenylene and polypyrrole	474
8.2.2	Organic metals: charge-transfer complexes	474
8.3	Superconductivity	476
8.3.1	The property of zero resistance	476
8.3.2	Perfect diamagnetism; the Meissner effect	478
8.3.3	Critical temperature $T_c$ , critical field $H_c$ and critical current $J_c$	478
8.3.4	Type I and type II superconductors: the vortex (mixed) state	480
8.3.5	Survey of superconducting materials	481
8.3.6	Crystal chemistry of cuprate perovskites	484
8.3.7	$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , YBCO	486
8.3.7.1	Crystal structure	486
8.3.7.2	Atom valences and the superconducting mechanism	488
8.3.7.3	Oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	488
8.3.7.4	Determination of oxygen content, $7-\delta$	490
8.3.8	Fullerides	491
8.3.9	Applications of superconductors	491
8.4	Semiconductivity	492
8.4.1	Elemental and compound semiconductors with diamond and zinc blende structures	494
8.4.2	Electrical properties of semiconductors	496
8.4.3	Oxide semiconductors	498
8.4.4	Applications of semiconductors	499
8.5	Ionic Conductivity	502
8.5.1	Alkali halides: vacancy conduction	503
8.5.1.1	Activation energy for ion hopping: geometric considerations	504
8.5.1.2	Ionic conductivity of NaCl crystals	506
8.5.1.3	Extrinsic conductivity in NaCl: control by aliovalent doping	507
8.5.2	Silver chloride: interstitial conduction	509
8.5.3	Alkaline earth fluorides	511
8.5.4	Solid electrolytes (or fast ion conductors, superionic conductors)	511
8.5.4.1	General considerations	511
8.5.4.2	$\beta$ -Alumina	513
8.5.4.3	Nasicon	519
8.5.4.4	Hollandites and priderites	519
8.5.4.5	Silver and copper ion conductors	521
8.5.4.6	Fluoride ion conductors	523
8.5.4.7	Oxide ion conductors	524
8.5.4.8	$\text{Li}^+$ ion conductors	528
8.5.4.9	Proton conductors	532
8.5.4.10	Mixed ionic/electronic conductors	532
8.5.4.11	Applications of solid electrolytes and mixed conductors	533
8.6	Dielectric Materials	547
8.6.1	From dielectrics to conductors	550
8.7	Ferroelectrics	553
8.8	Pyroelectrics	558
8.9	Piezoelectrics	558
8.10	Applications of Ferro-, Pyro- and Piezoelectrics	559

<b>9 Magnetic Properties</b>	<b>563</b>
9.1 Physical Properties	563
9.1.1 Behaviour of substances in a magnetic field	564
9.1.2 Effects of temperature: Curie and Curie–Weiss laws	566
9.1.3 Magnetic moments	567
9.1.4 Mechanisms of ferro- and antiferromagnetic ordering: superexchange	570
9.1.5 Some more definitions	571
9.2 Magnetic Materials, their Structures and Properties	572
9.2.1 Metals and alloys	572
9.2.2 Transition metal monoxides	576
9.2.3 Transition metal dioxides	577
9.2.4 Spinels	577
9.2.5 Garnets	580
9.2.6 Ilmenites and perovskites	581
9.2.7 Magnetoplumbites	582
9.3 Applications: Structure–Property Relations	582
9.3.1 Transformer cores	583
9.3.2 Permanent magnets	583
9.3.3 Magnetic information storage	584
9.4 Recent Developments	586
9.4.1 Magnetoresistance: giant and colossal	586
9.4.2 Multiferroics	587
<b>10 Optical Properties: Luminescence, Lasers and Transparent Conductors</b>	<b>589</b>
10.1 Visible Light and the Electromagnetic Spectrum	589
10.2 Sources of Light, Thermal Sources, Black Body Radiation and Electronic Transitions	589
10.3 Scattering Processes: Reflection, Diffraction and Interference	592
10.4 Luminescence and Phosphors	592
10.5 Configurational Coordinate Model	594
10.6 Some Phosphor Materials	596
10.7 Anti-Stokes Phosphors	597
10.8 Stimulated Emission, Amplification of Light and Lasers	598
10.8.1 The ruby laser	600
10.8.2 Neodymium lasers	601
10.8.3 Semiconductor lasers and the light-emitting diode, LED	602
10.9 Photodetectors	604
10.10 Fibre-Optics	606
10.11 Solar Cells and Photovoltaics	607
10.12 Transparent Conducting Oxides, TCOs, Smart Windows and Energy Management of Buildings	610
10.12.1 Indium tin oxide, ITO	610
10.12.2 Applications	614
10.12.3 p-type TCOs	616
10.13 Photonic Crystals, Photonic Bandgaps and Opals	616

<b>11 Heterogeneous Materials, Electroceramics and Impedance Spectroscopy</b>	<b>619</b>
11.1 Homogeneous and Heterogeneous Solids	619
11.2 Resistivities and Permittivities of Materials; The Parallel <i>RC</i> Element	621
11.3 Impedance Formalisms, Alternating Currents and Equivalent Circuits	624
11.4 Applications of Impedance Spectroscopy	634
<b>12 Thermal and Thermoelectric Properties</b>	<b>647</b>
12.1 Thermoelectric Effects	647
12.1.1 Thermocouples	650
12.1.2 Thermoelectric power generation	653
12.2 Thermal Properties: Heat Capacity, Thermal Conductivity, Thermal Expansion	656
12.2.1 Heat capacity	656
12.2.2 Thermal conductivity	658
12.2.3 Thermal expansion	660
<b>13 Functional Materials: Some Important Examples</b>	<b>663</b>
13.1 $\text{TiO}_2$ : Rutile, Anatase and Other Ti-O Phases	663
13.2 $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ , Mayenite: An Oxide Ion Conductor, Component of Cement and a Superconducting Electride	680
13.2.1 2D electrides	684
13.3 Zinc Oxide, $\text{ZnO}$ for Varistor and Optoelectronic Applications	685
13.4 Two-dimensional Structures: MXenes	689
13.5 Low-dimensional Solids: Graphene, BN, Transition Metal Dichalcogenides and Black Phosphorus	692
<b>14 Glass</b>	<b>697</b>
14.1 Factors That Influence Glass Formation	698
14.1.1 Viscosity	698
14.1.2 Structural effects: Zachariasen's rules	698
14.1.3 Other structural and bonding factors	699
14.2 Thermodynamics of Glass Formation; the Behaviour of Liquids on Cooling	700
14.3 Kinetics of Crystallisation and Glass Formation	703
14.4 Structure of Glasses	706
14.4.1 Vitreous silica and stochasticity	706
14.4.2 Silicate glasses	707
14.4.3 Vitreous $\text{B}_2\text{O}_3$ and borate glasses	709
14.5 Liquid Immiscibility and Phase Separation in Glasses	710
14.5.1 Structural theories of liquid immiscibility	711
14.5.2 Thermodynamics of liquid immiscibility	711
14.5.3 Mechanisms of phase separation: nucleation and growth; spinodal decomposition	712
14.6 Viscosity of Glasses and Melts	715
14.7 Electrical (Ionic) Conductivity of Glass and the Mixed Alkali Effect	718
14.8 Bonds, Bands and Semiconducting Glasses	721

14.8.1	Chalcogenide glasses	721
14.8.1.1	Sulphur	722
14.8.1.2	Selenium	722
14.8.1.3	Tellurium	722
14.8.1.4	More complex chalcogenide glasses: optical properties	722
14.8.2	Electrical properties	724
14.8.3	The photocopying process	725
14.8.4	Electrical switching and memory effects	725
14.9	Mechanical Properties and Strengthening of Glass	727
14.10	Commercial Silicate and Borate Glasses	728
14.10.1	Optical properties	730
14.11	Metallic Glasses	730
14.12	Fluoride Glasses	733
14.13	Glass-Ceramics	736
14.13.1	Some important glass-ceramic compositions	738
14.13.2	Properties of glass-ceramics	739
14.13.3	Applications of glass-ceramics	739
14.14	Bioglasses	740
<b>15</b>	<b>Structural Materials: Cement, Refractories and Structural Ceramics</b>	<b>743</b>
15.1	Cements	743
15.1.1	Manufacture of Portland cement	744
15.1.2	Phase diagram considerations	745
15.1.3	Polymorphism and crystal structures of the calcium silicates and aluminates	747
15.1.4	Silicate chemistry and silicate structures	749
15.1.5	Hydration of Portland cement	752
15.1.6	Types of Portland cement	754
15.1.7	Alkali activation and geopolymers	755
15.1.8	Autoclaved products	757
15.1.9	Aluminous cement, high alumina cement and refractory concrete	757
15.1.10	Macro-defect-free (MDF) Cement	759
15.1.11	Acid-base cements: oxychloride (Sorel) and glass-ionomer cements	760
15.2	Refractories and Structural Ceramics	761
15.2.1	Microstructure or texture of refractories and ceramics	761
15.2.2	Refractory materials and structural ceramics	765
<b>16</b>	<b>Oxides of the Elements, Their Properties and Uses</b>	<b>771</b>
16.1	Oxides of s-Block Elements	771
16.2	Acid-Base Classification of Oxides	773
16.3	Oxides of p-Block Elements	773
16.4	Oxides of d-block (Transition) Elements	774
16.5	Oxides of Lanthanides and Actinides	776
16.6	Oxides of the Elements Overview	776
<b>Appendix A:</b>	<b>Interplanar Spacings and Unit Cell Volumes</b>	<b>795</b>
<b>Appendix B:</b>	<b>Model Building</b>	<b>797</b>

<b>Appendix C: Geometrical Considerations in Crystal Chemistry</b>	<b>801</b>
<b>Appendix D: The Elements and Some of Their Properties</b>	<b>805</b>
<b>Appendix E: The 32 Crystallographic Point Groups</b>	<b>811</b>
<b>Appendix F: The Arrhenius Equation for Ionic Conductivity</b>	<b>815</b>
<b>Appendix G: A Guide to the Use of Electrode Potentials</b>	<b>819</b>
<b>Further Reading</b>	<b>823</b>
<b>Questions</b>	<b>837</b>
<b>Index</b>	<b>851</b>