

Functional and Smart Materials

Structural Evolution and Structure Analysis

Contents

Part I

STRUCTURE AND STRUCTURAL EVOLUTION

1. Structure, Bonding and Properties

- 1.1 Crystal structure
- 1.2 Structure and chemical composition
 - 1.2.1 Stoichiometric phases
 - 1.2.2 Non-stoichiometric phases
- 1.3 Coordination number and coordination polyhedron
- 1.4 Isotypism and polymorphism
- 1.5 Structure and chemical bonding
 - 1.5.1 Bonding and ion radius
 - 1.5.2 Lattice energy of an ionic compound
 - 1.5.3 Geometric consideration of a structure
 - 1.5.4 The rules of Pauling and Baur
 - 1.5.5 Covalent bonding
- 1.6 Ligand field theory
 - 1.6.1 Octahedral coordination
 - 1.6.2 Tetrahedral coordination
 - 1.6.3 Square coordination
- 1.7 Ligand field stabilization energy
- 1.8 Coordination polyhedra of transition metals
- 1.9 Molecular orbital theory of bonding
 - 1.9.1 Molecular orbitals
 - 1.9.2 Hybridization
- 1.10 Band theory
 - 1.10.1 The Peierls distortion
 - 1.10.2 Two- and three-dimensional bonds
- 1.11 Mixed valent compounds and functional materials
 - 1.11.1 Class I compounds
 - 1.11.2 Class II compounds
 - 1.11.3 Class III compounds
- 1.12 Structure transformation and stability
 - 1.12.1 Phase diagram
 - 1.12.2 Thermodynamic stability
- 1.13 Properties of materials
 - 1.13.1 Mechanical Property
 - 1.13.2 Magnetic property
 - 1.13.3 Piezoelectric property

- 1.13.4 Ferroelectric property
- 1.13.5 Optical property
- 1.13.6 Electric property
- 1.14 Structure and property
- 1.15 Functional materials
 - 1.15.1 Characteristics of functional materials
 - 1.15.2 Structural evolution and functionality
- 1.16 Summary

- 2. Sodium Chloride and Rutile Related Structure Systems
 - 2.1 Rock salt structure
 - 2.2 Non-stoichiometric compounds with sodium chloride structure
 - 2.3 Rutile structure and its family
 - 2.4 Characteristics of rutile structures
 - 2.4.1 Apex-sharing
 - 2.4.2 Edge-sharing
 - 2.4.3 Face-sharing
 - 2.5 Evolution of rutile-type structures
 - 2.6 Non-stoichiometry and crystallographic shear planes
 - 2.7 Summary

- 3. Perovskite and Related Structure Systems
 - 3.1 Characteristics of ABO_3 type perovskite structure
 - 3.1.1 Vertex-sharing of oxygen octahedra
 - 3.1.2 Unit cell by taking A cation as the origin
 - 3.1.3 Oxygen cubic close-packing
 - 3.1.4 Anion close-packing and formation of tetrahedron and octahedron
 - 3.2 Possible types of anion-deficient perovskite structures
 - 3.2.1 The 14 fundamental structure units
 - 3.2.2 Constructing the family of perovskite related structures
 - 3.3 The tolerance factor
 - 3.4 Functional materials with perovskite-like structures
 - 3.4.1 Ferroelectricity and ferroelectric compounds
 - 3.4.2 Ferromagnetism and ferromagnetic compounds
 - 3.4.3 Insulator to conductor transition
 - 3.4.4 Conductive perovskites
 - 3.4.4.1 Valence disproportionality
 - 3.4.4.2 Dimensionality
 - 3.4.4.3 Building the structures of high temperature superconductors using perovskite structure units
 - 3.4.5 Magnetostrictive, electrostrictive and piezoelectric actuator materials
 - 3.4.6 Optically switchable compounds
 - 3.5 Doping and oxygen vacancies
 - 3.6 Giant magnetoresistance (GMR) and colossal magnetoresistance (CMR)
 - 3.7 Oxygen migration and ionic conductivity of perovskites

3.8	Anion deficiency induced perovskite to brownmillerite structural evolution	
3.9	Ordered structural evolution introduced by cation substitution	
3.10	Sodium chloride, rutile and perovskite structures	
3.10.1	Linkage and comparison	
3.10.2	Constructing new materials by tailoring	
3.11	Summary	
4.	Fluorite-Type and Related Structure Systems	
4.1.	Basic fluorite structure	
4.2	Fluorite structure with anion deficiency	
4.2.1	Oxygen migration in fluorite structure	
4.2.2	Modules of fluorite structure with oxygen deficiency	
4.2.3	Pyrochlores and C-type rare earth sesquioxide structures	
4.3	Characteristics of fluorite and fluorite-related structures	
4.3.1	Thermodynamic property	
4.3.2	Surface character of rare earth oxides	
4.3.3	Disproportionation of rare earth high oxides	
	Switchable chemical reaction as an oxygen pump	4.3.4
4.4	Structural and compositional principles of rare earth homologous higher oxides	
4.4.1	Compositional principle of the homologous phases	
4.4.2	The modular juxtaposition rules	
4.4.3	Building supercell structure using modules	
4.5	Applications of the juxtaposition rules to known structures	
4.5.1	R_7O_{12} phase with $n = 7$ and $m = 1$	
4.5.2	R_9O_{16} phase with $n = 9$ and $m = 1$	
4.5.3	$R_{11}O_{20}$ phase with $n = 11$ and $m = 1$	
4.5.4	$R_{40}O_{72}$ phase with $n = 40$ and $m = 4$	
4.5.5	$R_{24}O_{44}$ phase with $n = 24$ and $m = 2$	
4.6	Predicting undetermined structures using the proposed modules	
4.6.1	β -polymorph with $m = 4$	
4.6.2	Undetermined structure with $n = 19$	
4.6.3	Undetermined structure with $n = 16$	
4.6.4	Undetermined structure with $n = 62$ and $m = 6$	
4.6.5	Non-stoichiometric α -phase	
4.7	Ternary mixed rare earth oxides	
4.7.1	Rare earth mixed ternary oxides and oxygen storage	
4.7.2	Cation coordination number and arrangements of modules	
4.8	Perovskite, fluorite structures and spinel structures	
	Structure comparison	4.8.1
4.8.2	Superexchange interaction and magnetism	
4.9	Summary	
5.	From Structural Units to Materials Engineering via Soft-Chemistry	

- 5.1 Principle of soft chemistry
- 5.2 Sol-gel process
- 5.3 Colloidal route for preparation of monodispersive spherical particles
- 5.4 Intercalation and pillaring processes
- 5.5 Self-assembled nanocrystal engineered superlattice thin films
 - 5.5.1 Passivated metal nanocrystals
 - 5.5.2 Passivated semiconductors nanocrystals
 - 5.5.3 Passivated magnetic nanocrystals
 - 5.5.4 Magnetic Co particles
 - 5.5.5 Magnetic iron oxides
- 5.6 Preparation of nanoparticles by aerosol technique
- 5.7 Summary

Part II

STRUCTURE CHARACTERIZATIONS

6. Electron Crystallography for Structure Analysis

- 6.1 Electron diffraction in structure analysis
 - 6.1.1 Single scattering theory
 - 6.1.2 Reciprocal space
 - 6.1.3 Bragg's law and Ewald sphere
 - 6.1.4 Indexing electron diffraction patterns
 - 6.1.5 Diffraction from twinned crystals
- 6.2 Diffraction contrast and defect analysis
 - 6.2.1 Defects and dislocations in materials
 - 6.2.2 Diffraction contrast
 - 6.2.3 Two-beam condition for imaging defects and dislocations
 - 6.2.4 Determination of Burgers vector
 - 6.2.5 Weak beam imaging
- 6.3 Atomic-resolution structure imaging and structure analysis
 - 6.3.1 Phase contrast
 - 6.3.2 Abbe's imaging theory
 - 6.3.3 Aberration and information transfer in TEM
 - 6.3.4 Contrast transfer function and image resolution
 - 6.3.5 Envelope function and information transfer
 - 6.3.6 Source coherence in lattice imaging
 - 6.3.7 Projected charge density approximation
 - 6.3.8 Multislice theory for transmission electron imaging
 - 6.3.9 Image simulation and structure determination
 - 6.3.10 Image calculation of imperfect crystal and interface
 - 6.3.11 Energy-filtered electron lattice imaging
 - 6.3.12 Limitation of HRTEM
- 6.4 Electron holography
 - 6.4.1 Principle of off-axis holography in TEM
 - 6.4.2 Improvement of image resolution
 - 6.4.3 Imaging electrostatic field and charge distribution

- 6.4.4 Imaging spontaneous polarization at domain boundaries in ferroelectrics
- 6.4.5 Imaging magnetic domains and flux lines
- 6.5 Convergent beam electron microdiffraction
 - 6.5.1 Symmetry analysis
 - 6.5.2 Measurement of lattice parameters
 - 6.5.3 Bloch wave theory and quantitative CBED
 - 6.5.4 Solid state bonding and charge redistribution
 - 6.5.5 Determination of Burgers vector
 - 6.5.6 Measurement of specimen thickness
- 6.6 Summary

- 7. Structure analysis of functional materials
 - 7.1 Interface and grain boundary analysis
 - 7.1.1 Kikuchi pattern and grain boundary analysis
 - 7.1.2 General description of a grain boundary
 - 7.1.3 The O-lattice theory
 - 7.1.4 Coincidence-site lattice theory
 - 7.2 Modulation and domain structure
 - 7.2.1 Structural modulation
 - 7.2.2 Domains formed by anisotropic crystal structure
 - 7.2.3 Boundaries of structure domains
 - 7.3 Superstructure and long-range ordering
 - 7.3.1 3-D superstructure analysis by a double-pattern technique
 - 7.3.2 3-D superstructure analysis by a single-pattern technique
 - 7.3.4 Long-range ordering of cation substitutions
 - 7.4 Oxygen vacancies and short-range ordering
 - 7.4.1 Kinematical diffraction theory of diffuse scattering
 - 7.4.2 Geometrical description of diffuse scattering
 - 7.4.3 Calculation of short-range ordering parameter
 - 7.4.4 HRTEM study of short-range order
 - 7.5 Effects of substrate on thin film growth
 - 7.5.1 Lattice mismatch and interface dislocations
 - 7.5.2 Nucleation and growth of defects from substrate surfaces
 - 7.5.3 Linkage of domain boundaries with interface dislocations
 - 7.5.4 Linkage of interface dislocations with planar defects
 - 7.6 In-situ observation of structure evolution
 - 7.6.1 Temperature driven structure transformation
 - 7.6.2 Electric field driven structure transformation
 - 7.6.3 Magnetic moment of the specimen
 - 7.7 Failure analysis of devices
 - 7.8 Imaging surfaces of oxides
 - 7.9 Summary

- 8. Chemical and Valence Structure Analysis of Functional Materials
 - 8.1 Inelastic excitation processes in electron scattering

- 8.2 Energy dispersive x-ray microanalysis (EDS)
 - 8.2.1 Composition analysis
 - 8.2.2 Atom location by channeling enhanced microanalysis (ALCHEMI)
- 8.3 Valence excitation EELS
 - 8.3.1 Classical electron energy-loss theory
 - 8.3.2 Surface plasmon excitation
 - 8.3.3 Measurement of dielectric function
- 8.4 Atomic inner shell excitation in EELS
 - 8.4.1 Composition analysis
 - 8.4.2 Near edge fine structure and bonding in crystals
- 8.5 Quantitative determination of valences in a mixed valent compound
 - 8.5.1 White lines of transition metals
 - 8.5.2 The occupation number of the d-band electrons
 - 8.5.3 White line intensity and intrinsic magnetic moment
 - 8.5.4 Double derivative spectrum for calculation of white line intensity
- 8.6 Nano-probe analysis of interfaces and grain boundaries
- 8.7 Chemical sensitive imaging in STEM
- 8.8 Energy filtered electron imaging in TEM
 - 8.8.1 Composition-sensitive imaging using valence-loss electrons
 - 8.8.2 Composition-sensitive imaging using inner-shell ionization edge electrons
 - 8.8.3 Mapping of bonding and valence state
- 8.9 Phonon scattering and chemical sensitive imaging
 - 8.9.1 'Z-contrast' imaging in STEM
 - 8.9.2 High-angle dark-field conical scan imaging in TEM
- 8.10 Conjunction use of various techniques for structure refinement of $\text{La}_8\text{Sr}_8\text{Co}_{16}\text{O}_{36}$ - an example
- 8.11 Summary

APPENDIXES

- A: Physical constants, electron wavelengths and wave numbers
- B1: Crystallographic structure systems
- B2: FORTRAN program for calculating crystallographic data
- C: Electron diffraction patterns for several types of crystal structures
- D: FORTRAN program for calculating single valence-loss EELS spectra in TEM

References

Index