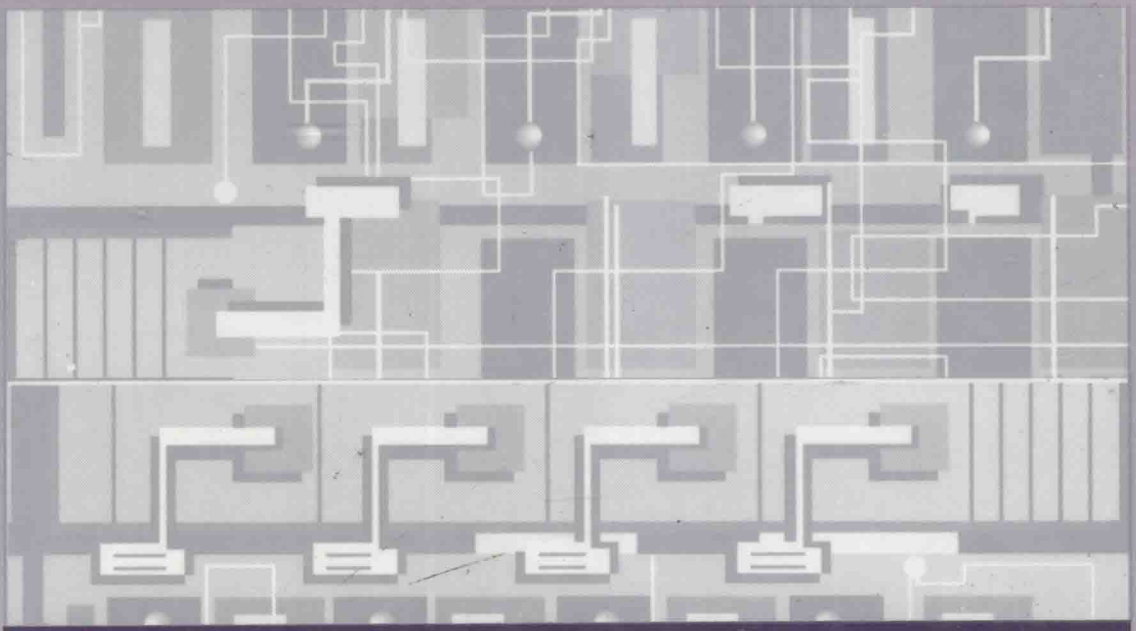
Functional and Smart Materials

Structural Evolution and Structure Analysis



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Functional and Smart Materials

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To all of our family members

Foreword

At the end of this century, the technological importance of oxides are growing extremely fast. Most of the information is transported by optical fibers because light can carry more information than conventional electromagnetic waves. This implies new microlasers and new microamplifiers where polyoxides, such as lithium niobate crystals, are required. Research on these crystals is experiencing a superfast development and many new discoveries have reached the industrial stage of large scale production. As sparked by the extraordinary discovery of high temperature superconductors in 1986, growth and characterization of oxides are a forefront research field in materials science. Less spectacular, but very important, also are the progresses made during the last thirty years in the field of industrial ceramics, for instance the dramatic improvements obtained with stabilized zirconia. Progresses are made daily in the field of "Research and Development" with oxides presenting some special physical property and functionality. The largest domain of interest is presently a possible coupling between at least two different kinds of properties (i.e., the smart structure). These progresses have been possible because of the fundamental understanding of their structure and microstructure. In the book by Z. L. Wang and Z. C. Kang one can find a very interesting concentration of basic physical properties of the most important polyoxides, related to their structures (and microstructures) and evolution behavior. The approach of Z. L. Wang and Z. C. Kang is very interesting and rather new: they have classified oxides through their structures and their physical properties. Rock, salt, rutile, fluorite, perovskite and many other related (or mixed) structure types are comprehensively described in the first four chapters with an emphasis on the connections among different structure systems. The fifth chapter is about the important process known as "Soft Chemistry" or "Chimie Douce". The second part, Chapters 6 through 8, are devoted to the optimal techniques and technologies used for study of these compounds and their physical properties. This book is unique because it focuses specifically on the intrinsic connections among several crystal structure systems and their evolution behavior. It relates the basic principles for molecular and structural design of functional materials to the fundamental structure modules. These materials are described from the mixed-valence and stoichiometry points of view to understand their structural transformation and the evolution of different materials systems.

The mixed valences of transition and rare earth metals have been shown as a fundamental for oxides with specific functionalities. There are numerous books describing the properties, preparations, electronic and crystal structures of transition, rare earth metals and their oxides. This book fills a gap in that field, not only because it focuses on the role played by the evolution of crystal structures in functional materials, but also gives the solution of structure determination through advanced techniques such as spectroscopy and transmission electron microscopy. Because this specific approach has been followed I am confident this book will be a basic reference in the domain of oxides which are to be the basis of functional and smart materials.

C. Boulesteix
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Preface

Functional materials, a new emerging materials system, have attracted the interests of many scientists, since they are synthesized to perform specific functionality. Functional materials include but are not limited to smart materials, and they cover a large range of materials with important applications in modern and future technologies. To be unique, this book is not a compiled list of various functional materials, rather it is on the intrinsic connection and evolution behavior among and in different structure systems which are frequently observed in oxide functional materials. Each structural system is described from the basic modules that are the building blocks for constructing all of the related structures. The structural evolution is linked with mixed valences of rare earth and transitional metal elements, and this is shown to be the fundamental principle for producing new materials with unique functionality. The book aims to explore the fundamental structural mosaics that likely lead to some new routes for synthesizing new functional materials. The book is also unique in the way that it integrates structural evolution with structure analysis using transmission electron microscopy and associate techniques.

We have written this book for advanced graduate students and scientists who are interested in studying and developing functional materials. The intended readers are materials scientists, solid state chemists (material chemists), electron microscopists, mineralogists, and solid state physicists (material physicists). The book also fulfills the need as a text book for advanced research and education in oxide functional materials and transmission electron microscopy.

This book was written based on our research experience on the subject. Chapters 2–4 were primarily written by ZCK. The Introduction section, Chapters 6–8 and all of the Appendixes were written by ZLW. Chapters 1 and 5 were co-authored by ZCK and ZLW. ZLW was responsible for organizing and editing the entire manuscript, and he was also cited as liason during the publication process.

We would like to express gratitude to our collaborators related to the research described in this book. Thanks to Professor L. Eyring, a pioneer in the field, for your advice and encouragement. Thanks also go to Professor C. Boulesteix, Dr. D.M. Kroeger, Dr. Jiming Zhang and Professor R.L. Whetten for collaborative research in the past few years. We are also grateful to those who kindly permit us to use their data for illustrating the text, and each of them is acknowledged in the corresponding figure caption.

Finally, our heartfelt gratitude goes to our wives, children, and parents, for their constant encouragment, support and understanding. Their support and help are indispensable for finishing this book.

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Symbols and Definitions

Listed below are the symbols frequently used in this book. All quantities are defined in SI units except that Angstrom (Å) is used occasionally for convenience.

$\mathbf{R}_n$	Lattice displacement vector
E_c	Lattice energy
A	Madelung constant
r_M	Cation radius
r_X	Anion radius
p_i	Coordination number
s_i	electrostatic bond strength
z_j	Charge of the jth anion
d(MX)	Bond length
Δ_0	Energy gap between t and e orbitals in octahedral coordination
Δ_t	Energy gap between t and e orbitals in tetrahedral coordination
ψ_i	Molecular orbit
ϕ_i	Atom wave function
S_{12}	Overlap integral
α_v	Valence delocalization coefficient
ΔG	Free enthalpy of reaction
ΔH	Transition enthalpy
ΔS	Transition entropy
χ	Magnetic susceptibility
M	Magnetization
H	Magnetic field
M_r	Remnant magnetization
H_c, E_c	Coercive force/field
P_s	Spontaneous polarization
T_c	Ferromagnetic transition temperature (or Curie temperature)
T_g	Superparamagnetic freezing temperature
$N(E)$	Density of states
μ_B	Bohr magneton

w_b	Band gap
U_b	Transfer energy
r_X	Radius of anions
r_M	Radius of cation
χ_X	Electronegativity
μ	Chemical potential
η_X	Hardness of atom X
h	Planck's constant
$\hbar$	$= h/2\pi$
c	Speed of light in vacuum
m_0	Rest mass of electron
m_e	Mass of electron with relativistic correction
e	Absolute charge of electron
U_0	Accelerating voltage of electron microscope
λ	Electron wavelength in free space
$\mathbf{p}$	Momentum of incident electron
$\mathbf{K}_0$, $\mathbf{K}$	Electron wave-vectors
θ	Electron scattering semiangle
f_α^e	Electron scattering factor of αth atom
f_α^x	X-ray scattering factor of αth atom
$\mathbf{FT}$	Fourier transform from real space to reciprocal space
$\mathbf{FT}^{-1}$	Inverse Fourier transform
$\mathbf{r}$	$= (x, y, z)$ real space vector
$\mathbf{b}$	$= (x, y)$ real space vector
$\mathbf{g}$ (or $\mathbf{h}$)	Reciprocal lattice vector
$\mathbf{u}$, τ	Reciprocal space vector
$V(\mathbf{r})$	Electrostatic potential distribution in crystal
$V_\kappa(\mathbf{r})$	Electrostatic potential of κth atom
$\rho_\kappa(\mathbf{r})$	Electron density distribution of κth atom
$\mathbf{s}$	Scattering vector, $\mathbf{s} = \mathbf{u}/2$
s	$= (\sin\theta)/\lambda$
Z	Atomic number
V_g	Fourier coefficient of crystal potential
$V_\alpha(\mathbf{g})$	Fourier transform of αth atom in unit cell
$\exp(-W_\alpha)$	Debye–Waller factor of αth atom
Ω	Volume of unit cell
$\mathbf{r}_\alpha$	$= \mathbf{r}(\alpha)$, position of αth atom within unit cell
$\mathbf{R}_n$	Position vector of nth unit cell
$\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$	Base vectors of unit cell
$\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$	Base vectors of reciprocal lattice vector
$\mathbf{a}_s$, $\mathbf{b}_s$, $\mathbf{c}_s$	Base vectors of superstructure unit cell
$\mathbf{a}_s^*$, $\mathbf{b}_s^*$, $\mathbf{c}_s^*$	Base vectors of reciprocal lattice vectors for the superstructure
θ_g	Bragg angle
d_g	Interplanar distance
$\otimes$	Convolution calculation
T_{obj}	Transfer function of objective lens
A_{obj}	Shape function of objective aperture
C_s	Spherical aberration coefficient of objective lens

Δf	Defocus of objective lens
E	$= eU_0[1 + eU_0/2m_0c^2]$, energy of incident electron
U_g	Fourier coefficient of the modified potential U
v	Velocity of incident electron
γ	$= (1-(v/c_0)^2)^{1/2}$, relativistic correction factor
$U(\mathbf{r})$	$= (2\gamma m_0 e/h^2)V(\mathbf{r})$, modified crystal potential
$\Psi(\mathbf{r})$	Electron wave function
$\Phi(\mathbf{r})$	Electron wave function excluding $\exp(2\pi i\mathbf{K} \cdot \mathbf{r})$ factor, $\Phi(\mathbf{r})=\Psi(\mathbf{r}) \exp(-2\pi_i\mathbf{K} \cdot \mathbf{r})$
$B_i(\mathbf{r})$	ith branch Bloch wave
$\mathbf{k}^{(i)}$	Wave vector of ith Bloch wave
α_i	Superposition coefficients of Bloch waves
$C_g^{(i)}$	Eigenvector of ith Bloch waves
ν_i	Eigenvalue of ith Bloch waves
ξ_g	Two-beam extinction distance
d	Thickness of crystal slab
$\phi_g(\mathbf{r})$	Amplitude of $\mathbf{g}$ reflection
$\mathbf{R}(\mathbf{r})$	Static displacement vector of atoms in imperfect crystal
$\mathbf{b}_B$	Burgers vector of dislocations
$\mathbf{u}_D$	Direction of dislocation line
$V_p(\mathbf{b})$	Projected crystal potential along z direction
Δf_s	Scherzer defocus
Δf_c	Defocus due to chromatic aberration
R_s	Scherzer resolution
$\gamma(\mathbf{b})$	Coherence function
σ	$= \pi e\gamma/\lambda E = 1/\hbar v.$
Δz	Thickness of crystal slice
$P(\mathbf{b}, \Delta z)$	Propagation function of slice with thickness Δz
Q_n	Phase grating function of slice with thickness Δz
$\mathbf{T}$	Transformation matrix
$\mathbf{A}$	Vector potential of magnetic field
$\mathbf{B}$	Magnetic field
$\mathbf{R}_n$	$= \mathbf{R}(n)$, position of nth unit cell
T	Temperature
V_c	Volume of crystal
$\hat{z}$	Unit vector along z axis
$\mathbf{r}_\alpha$	Position of αth atom in unit cell
μ_A	X-ray absorption coefficient
I_A	Integrated x-ray line intensity
ω_A	Fluorescence yield
n_A	Number of A element per unit volume
σ_A	Ionization cross section of the inner shell
a_A	Fraction of the K, L, or M line intensity measured by the detector
γ_A	Detector efficiency
A_b	Absorption factor
k_A	K factor for x-ray microanalysis
n_X	Concentration of impurity X
C_X	Fraction of impurity X in B atom sites

$\mathbf{E}$	Electric field
$\mathbf{D}$	Displacement vector
ϑ_E	Characteristic angle of inelastic scattering
Λ	Mean-free path length of inelastic electron scattering
ε, $(\omega, \mathbf{q})$	Dielectric function of solid
$d^2P_v/dz\,d\omega$	Differential excitation probability of valence states
ρ	Free charge density function
ω_p	Resonance frequency of the plasmon
σ_I	Integrated ionization cross section
β	Collection semiangle of the EELS spectrometer
Δ	Energy width of the integration window

SIGN CONVENTIONS

Free-space plane wave $\exp\,[2\pi i\mathbf{K}\cdot\mathbf{r} - i\omega t]$

Fourier transforms

Real space to reciprocal space	$F(\mathbf{u}) = \int d\mathbf{r}\,\exp[-2\pi i\mathbf{u}\cdot\mathbf{r}]f(\mathbf{r}) \equiv \mathbf{FT}[f(\mathbf{r})]$
Reciprocal space to real space	$f(\mathbf{r}) = \int d\mathbf{u}\,\exp[2\pi i\mathbf{u}\cdot\mathbf{r}]F(\mathbf{u}) \equiv \mathbf{FT}^{-1}[F(\mathbf{u})]$

where the limits of integration are $(-\infty, \infty)$ unless otherwise specified.

ACRONYMS

ALCHEMI	Atom location by channeling-enhanced microanalysis
ADF	Annular dark field
BF	Bright field
bcc	Body-centered cubic
BZ	Brillouin zone
CBED	Convergent beam electron diffraction
c.n.	Coordination number
CSL	Coincident site lattice
CVD	Chemical vapor deposition
DF	Dark field
DOS	Density of states
DTA	Differential thermal analysis
EDS	Energy dispersive x-ray spectroscopy
EELS	Electron energy loss spectroscopy
ELNES	Energy loss near-edge structure
fcc	Face centered cubic
FWHM	Full width at half-maximum
GB	Grain boundary
HAADF	High-angle annular dark field
hcp	Hexagonal close packing
HOLZ	High-order Laue zone
HOMO	Highest occupied molecular orbital

HRTEM	High-resolution transmission electron microscopy
LACBED	Large-angle convergent beam electron diffraction
LFSE	Ligand field stabilization energy
LMR	Longitudinal magnetic recording
MOCVD	Metal organic chemical vapor deposition
MBE	Molecular beam epitaxy
NCS	Nanocrystal superlattices
PCM	Partial charge model
PMR	Perpendicular magnetic recording
PMN	$Pb(Mg,Nb)O_3$
PZT	$Pb(Zr,Ti)O_3$
REM	Reflection electron microscopy
RHEED	Reflection high-energy electron diffraction
RT	Room temperature
SAD	Selecting area diffraction
SC	Soft chemistry
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
TDS	Thermal diffuse scattering
WPOA	Weak phase object approximation
POA	Phase object approximation
ZOLZ	Zero-order Laue zone
1-D	One dimensional
2-D	Two dimensional
3-D	Three dimensional

Contents