FUNCTIONAL AND SMART MATERIALS -Structural evolution and structure analysis

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Introduction

Smart systems and smart materials Smart structures are a new emerging materials system which combines contemporary materials science with information science. The smart system is composed of sensing, processing, actuating, feedback, self-diagnosing and self-recovering subsystems. The system uses the functional properties of advanced materials to achieve high performances with capabilities of recognition, discrimination, and adjustification in response to a change of its environment. Each component of this system must have functionality, and the entire system is integrated to perform a self-controlled smart action, similar to a living creature who can "think", make judgment and take actions. A smart system can be considered as a design philosophy that emphasizes predictivity, adaptivity and repetivity. A smart system/structure is defined to be a non-biological physical structure having the following attributes: (1) a definite purpose; (ii) means and imperative to achieve that purpose; and (iii) a biological pattern of functioning (Spillman et al., 1996). Smart materials are a subset of the smart system, i.e. smart structures at the microscopic or mesoscopic scales. Smart system is a non-biological structure which means that the system functions as a biological system rather than the pattern of functioning of a Turning machine. A smart material is a physical structure having (i) a definite purpose, (ii) means of imperative to achieve that purpose, and (iii) the pattern of functioning of a universal computer or Turning machine. Such a material will generally include at least one structural element, some means of sensing the environment and/or its own state, and some type of processing and adaptive control algorithm. Science and technology in the 21st century will rely heavily on the development of new materials that are expected to respond to the environmental changes and manifest their own functions according to the optimum conditions. The development of smart materials will undoubtedly be an essential task in many fields of science and technology such as information science, microelectronics, computer science, medical treatment, life science, energy, transportation, safety engineering and military technologies. Materials development in the future, therefore, should be directed toward creation of hyperfunctional materials which surpass even biological organ in some aspects. The current materials research is to develop various pathways that will lead the modern technology toward the smart system.

Functional materials Functional materials are distinctly different from structural materials, and their physical and chemical properties are sensitive to a change in the environment such as temperature, pressure, electric field, magnetic field, optical wavelength, adsorbed gas molecules and the pH value. The functional materials utilize the native properties and functions of their

own to achieve an intelligent action. Functional materials cover a broader range of materlas than the smart materials illustrated above. Besides the materials belogning to the smart structure, any materials that have functionality are attributed to functional materials, such as the ferroelectricic BaTiO3, the magnetic field sensor of La1-xCaxMnO3, surface acoustic wave sensor of LiNbO3, liquid petroleum gas sensor of Pd-dopped SnO2, semiconductor light detectors (CdS, CdTe), high temperature piezoelectric Ta2O5, fast-ion conductor Y2(SnyTi1-y)2O7 (pyrochlore structure), the electric voltage induced reversible colouring of WO3, and high temperature superconductors etc. Functional materials cover a wide range of organic and inorganic materials. This book focuses only on oxide functional materials. In recent years, techniques for epitaxial crystal growth have made it possible to grow oxides and metal thin films on silicon substrates, and this is the first step to integrate functional materials with the logic system. Preparations of complex oxides with functionality are a key challenge for materials development. Searching new routes to prepare materials and understanding the relationship between the structures and the properties are equally important. A key requirement in preparations of materials is to control the structural and compositional evolution for achieving superior properties. "Soft chemistry" has shown a great success in fabricating functional and nanophase materials. Nanocrystal engineered materials are a new trend of materials research, aiming to improve the performances of materials by several orders of magnitudes.

Mixed valences and functionality Crystal structure usually refers to two aspects of information, one is the symmetry and distribution of atoms in the unit cell and the other is the bonding between atoms. Thermordynalically, the enthalpy of the system is determined by the bonding between atoms, while the entropy is determined by the atomic lattice configurations of the crystal. Thermodynamic rules select the possible stable phases, and the phase stability is strongly affected by bonding. A single element has a certain electron configuration. When several different elements form a molecule, the electronic structure of this cluster is very different from any of its original elemental configuration because of the transfer and/or sharing of valence electrons among atoms. In general, only the valence electrons are most critical to bonding, the distribution and motion of valence electrons are usually described by the molecular orbitals. These valence states and molecular orbits are responsible for the functional properties of the molecule. The ligand field theory is designed to describe the molecular structure of an atom cluster. When different elements are combined to form a crystalline solid in which the atoms or atom groups (or molecules) are bonded together to form a three-dimensional (3-D) structure with specified symmetries, the properties of the solid would depend on both the electronic structure of the atoms or atom groups and their spatial distribution. The molecular orbital theory and band structure theory are usually applied to elucidate the relationship between the structure and the properties. Based on the electron band structure, inorganic materials can be classified as conductors, semiconductors and insulators. If a change is made in the crystal structure so that the band gap is reduced or eliminated, a transition from an insulator to a conductor is possible. Modifying a crystal structure can be performed by changing either the spatial distribution of atoms (such as bonding angles, bonding lengths and symmetry of atom arrangement) or chemical

composition (such as from stoichiometry to nonstoichiometry). All these changes are referred to as structural evolution, which is closely related to the properties of the materials. Many functional properties of inorganic materials are determined by the elements with mixed valences in the structure unit, by which we mean that an element has two or more different valences while forming a compound. Valence mixture refers to a case in which several elements have different valences but each one only has a single valence. In the periodic table of fundamental elements, 40 elements can form mixed valent compounds, transition d-block elements and lanthanide (Eu, Yb, Ce, Pr, Tb etc.) are typical examples. Modern inorganic chemistry has shown that the oxidation state of any element can be modified under special conditions. Many oxide functional materials contain elements with mixed valences. This is a typical difference between the functional materials and the structural materials. This book is about the structural evolution of compounds containing mixed valent elements, such as transition and rare earth elements. The concept of mixed valent chemistry offers a pathway to design and synthesize new compounds with unique optical, electric, or magnetic properties. Research in functional materials in its broad sense always depends on the conception and synthesis of interesting novel mixed-valent compounds. The discovery of high temperature superconductor compounds is a fascinating successful example of the mixed valence chemistry. We believe that exploring the possible structures of mixed valent compounds and their evolution behaviors may lead to many pathways to synthesis new functional materials.

The scope of the book Searching for new functional materials is a challenge for the development of smart systems. To guide this searching, a clear understanding about the relationship between the physical properties and the atomic-scale structure of the materials is desperately needed. This book is about the intrinsic connections among several crystal structure systems commonly used in functional materials and their evolution behaviors. The book is not intended as a source for listing all the existing functional materials, instead its goal is to reveal the principles for engineering and controlling functional materials from the fundamental structure units. The functional materials are described from the mixed valences and stoichiometry points of view to understand the structural evolution and transformation of different materials systems. The mixed valent compounds are elucidated as the fundamentals for performing unique functionality. We have written this book with a strong conviction that functional materials system is a future direction of the multidisciplinary research involving physics, chemistry, materials science, electrical engineering and biological science, with an emphasis on molecular and unit cell designs. There are numerous books describing the properties, preparations, electronic structures and crystal structures of transition and rare earth metals and their oxides. To expert in the field, this book is written by addressing the issues that have not been described systematically in existing books. Our aim is to explain the intrinsic connections among different structures. The goal is to explore new routes for synthesizing functional materials from the fundamental structure building blocks (or modules). The book aims to illustrate not only the role played by crystal structure in property control of functional materials, but also the structure determination using advanced transmission electron microscopy and spectroscopy techniques. The latter also

has critical importance for device failure analysis in modern industry. Accordingly, the book is written into two parts. Part I concentrates on the structure and structural evolution of oxides functional materials belonging to NaCl-, rutile-, perovskite and CaF2-type structures and the related. Although our analysis is focused on the structure systems outlined above, spinel and corundum structures are also briefly described in these chapters except the wurtzite structure (BeO and ZnO) because of its limited evolution characteristics. Part II is on crystallographic and chemical structure characterizations of oxide functional materials, which are needed to understand the experimental approaches for exploring the structure evolution. Both parts are written to ensure the coherency of the whole book. Part I is composed of five chapters. In Chapter 1, fundamental concepts are introduced on crystallographic structures, chemical structures, bonding, molecular orbital and ligand field, mixed valences, materials properties and the fundamental characteristics of functional materials. This chapter is designed as the preliminary preparation for the discussions to be outlined in future chapters. The characteristics of functional materials are given for distinguish them from structural materials. Chapter 2 starts with the simplest oxides with NaCl structure for illustrating the stacking of cations and anions in constructing the unit cell. Then, rutile related structures are introduced with an emphasis on their structural evolution. Chapters 3 is on perovskite and related structures. The characteristics of the ABO3 perovskites are thoroughly analyzed to reveal the intrinsic connections among the A, B and O elements and the roles played by the octahedron in constructing the unit cells. The alternative stacking of the close-packed (AO3)4- and B layers is analyzed in detail, and a total of 14 fundamental structure units are extracted with introducing of anion deficiency, which are the building blocks for constructing the unit cells of complex functional materials. The tailoring of cation octahedra can give the structure of a variety of compounds. The typical properties of perovskites are also described and their relations with the crystal structure are elucidated. This chapter is the basis for understanding the mechanisms that control cation substitution, creation of oxygen vacancies and mixed valences in the perovskite family. Similarly, the fluorite related structures are analyzed in Chapter 4, and a total of 12 fluorite modules (or units) with anion deficiencies are proposed, which together with the perfect fluorite are the 13 basic building blocks for constructing the structures of rare earth homologoues higher oxides. Following the structural and compositional principles outlined by Kang and Eyring (1995, 1996), geometrical assembling of these modules can reproduce not only the known crystal structures of homologoues phases RnO2n-2m but, more importantly, predict the structures of some phases whose structures are unknown. This chapter proves that a complex superstructure can be disassembled into some fundamental modules, which can be derived at the first place from the basic fluorite structure. Therefore, by revealing the intrinsic connection among the same class of phases one may be able to predict and design new structures. The surface property and oxygen migration can be better understood from the view of module combination. At the end of Chapter 4, the structures of perovskite, fluorite and spinel are compared with each other and a brief introduction about spinel is given. Chapter 5 focuses on the introduction of soft-chemistry (sol-gel, pillaring and grafting, intercalation and deintercalation) for synthesizing and designing new materials based on the fundamental structure modules. The chapter aims to using the

understanding about structural evolution described in previous chapters to develop new materials systems that are expected to have functionality. Preparation of nanophase materials is also described with an emphasis on self-assembled nanocrystal superlattices (or arrays). This is a new trend of materials research on nanocrystal engineered (or patterned) materials. Part II is composed of Chapters 6-8. Chapter 6 aims to introduce the fundamentals of structure analysis using transmission electron microscopy and associated techniques, including electron diffraction, diffraction contrast for defect analysis, atomic resolution lattice imaging for interface studies, electron holography for studying ferroelectric and ferromagnetic materials, and convergent beam electron diffraction technique for mapping charge redistribution and bonding in crystalline materials. While introducing these fundamental techniques, our focus is on the applications of these techniques for the analysis of functional materials. This chapter also serves as an educational chapter to the readers who have different background in solid state chemistry, materials processing and structure analysis, for correctly using the available tools for solving the problems in oxide functional materials. The applications of the techniques introduced in Chapter 6 are described in Chapter 7 case-by-case to cover the structural characteristics of oxide functional materials, including grain boundaries, interfaces, domains, structure transformations and surfaces. Analysis of long-range superstructures and short-range order of point defects is the emphasis of this chapter because they are closely related to the structural evolution described in Chapters 2-4. Numerous examples are shown to illustrate the techniques for solving the structure problems belonging to functional materials. Chapter 8 focuses on the chemical and bonding analysis of mixed valent oxides at a high spatial resolution using the energy dispersive x-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS). The near edge fine structure observed in EELS is a sensitive technique for detecting the valence band structure from a small region, and it also allows the analysis of interface electronic structures. The observed white lines in EELS can be used to determine the occupations of the 3d and 4d orbitals (e.g., valence states) of transition and rare earth elements. This information together with the imaging and diffraction data from HRTEM can be applied to determine the ordered structure induced by ordered anion vacancies. Finally, it is emphasized that the structure information provided by imaging and diffraction techniques (Chapters 6 and 7) must be integrated with the chemical information provided by EDS and EELS. The structure refinement of an anion deficient phase $La_8Sr_8Co_{16}O_{36}$ is demonstrated as an example. A combination of TEM results with x-ray diffraction or neutron diffraction data and theoretical modeling as well is likely to give a unique and reliable solution to a material's problem. It is concluded that the structural evolution in a complex system is intrinsically dominated by the combinations of the fundamental structural modules. This is the focus of this book.