# Transition Metal Oxides

## Structure, Properties, and Synthesis of Ceramic Oxides

SECOND EDITION

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WILEY-VCH

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Second Edition

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# Preface to the Second Edition

We are gratified by the good reception to the first edition of this book. Clearly, the area of transition metal oxides is attracting increasing attention from the scientific community in the last few years. This is not entirely surprising considering that every other year there is a major development. Thus, since the publication of the first edition of this book, giant magnetoresistance or colossal magnetoresistance has been discovered in rare-earth manganates of the formula $Ln_{1-x}A_xMnO_3$ (Ln = rare earth, A = alkaline earth). There has been a spate of research papers in the literature on this subject. The study of giant magnetoresistance has also given rise to several new developments such as the charge ordering phenomenon in these oxides. We cover some of the salient aspects of the manganates in this edition. There has also been considerable work on superconducting cuprates, especially mercury derivatives. We have added new material on these cuprates as well as on oxyanion derivatives of cuprates and ladder compounds. It is noteworthy that, under pressure a ladder cuprate has been found to be superconducting. In addition, we have included some new aspects of synthesis of oxide materials including soft chemistry routes. With this new material and additional references, we trust that the second edition of the book will be found useful by a wide community of scientists working in materials science, ceramics, and condensed matter science.

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# Preface

Transition metal oxides constitute one of the most fascinating classes of inorganic solids, exhibiting a very wide variety of structures, properties, and phenomena. The unusual properties of transition metal oxides are due to the unique nature of the outer *d* electrons, the metal–oxygen bonding varying anywhere from nearly ionic to metallic. Transition metal oxides possessing several types of complex structure have been characterized in recent years. These include not only the well-known perovskite, spinel, pyrochlore, and hexagonal ferrite structures, but also the octahedral tunnel structures exhibited by bronzes and bronzoids, lamellar and low-dimensional structures, as well as three-dimensional mixed frameworks of octahedra and tetrahedra. Some of the oxides show ordered defect complexes or extended defects instead of isolated point defects; they also occur as shear and block structures or infinitely adaptive structures. Intergrowth of like structural units is commonly found in complex oxides. It has been possible to obtain the fine architectural details of complex transition metal oxides in terms of both the crystal structure and the ultramicrostructure because of the recent advances in diffraction and microscopic techniques.

The phenomenal range of electronic and magnetic properties exhibited by transition metal oxides is equally noteworthy. There are oxides with metallic properties (e.g., $RuO_2$, $ReO_3$, $LaNiO_3$) at one end of the range and oxides with insulating behavior (e.g., $BaTiO_3$) at the other. There are oxides that traverse both these regimes with change in temperature, pressure, or composition (e.g., $V_2O_3$, $La_{1-x}Sr_xVO_3$). Interesting electronic properties also arise from charge-density waves (e.g., $K_{0.3}MoO_3$), charge ordering (e.g.,

$Fe_3O_4$), and defect ordering (e.g., $Ca_2Mn_2O_5$, $Ca_2Fe_2O_5$). Examples are known of oxides with diverse magnetic properties: ferromagnetic (e.g., $CrO_2$, $La_{0.5}Sr_{0.5}MnO_3$), ferrimagnetic ($Fe_3O_4$, $MnFe_2O_4$), and antiferromagnetic (e.g., NiO, $LaCrO_3$). Many oxides possess switchable orientation states as in ferroelectric (e.g., $BaTiO_3$, $KNbO_3$) and ferroelastic [e.g., $Gd_2(MoO_4)_3$] materials. No discovery in the physical sciences has created as much sensation, however, as that of high temperature superconductivity in cuprates. Although superconductivity in transition metal oxides was known for some time, the highest $T_c$ reached till 1987 was around 13 K; we now have oxides with $T_c$ values in the region of 135 K. The discovery of high temperature superconducting oxides has focused worldwide interest on the chemistry and physics of transition metal oxides and has at the same time revealed the inadequacy of our understanding of these fascinating materials.

The unusual properties of transition metal oxides that distinguish them from metallic elements, covalent semiconductors, and ionic insulators arise from several factors. First, the oxides of *d*-block transition elements have narrow electronic bands, because of the small overlap between the metal *d* and oxygen *p* orbitals. The bandwidths are typically of the order of 1 or 2 eV (rather than 5–15 eV as in most metals). Electron correlation effects play an important role because of the narrow electronic bands. The local electronic structure can be described in terms of atomiclike states [e.g., $Cu^{1+}$ ($d^{10}$), $Cu^{2+}$ ($d^9$), and $Cu^{3+}$ ($d^8$) for Cu in CuO] as in the Heitler–London limit. The polarizability of oxygen is also of importance. The oxide ion $O^{2-}$ does not exactly describe the state of oxygen, and configurations such as $O^-$ have to be included, especially in the solid state. Species such as $O^-$, which are oxygen holes with a $p^5$ configuration instead of the filled $p^6$ configuration of $O^{2-}$, can be mobile and correlated. Many transition metal oxides are not truly three-dimensional, but have low-dimensional features. For example, $La_2CuO_4$ and $La_2NiO_4$ with the $K_2NiF_4$ structure are quasi-two-dimensional compared to $LaCuO_3$ and $LaNiO_3$, which are three-dimensional perovskites. Because of their varied features, it has not been possible to establish fully satisfactory theoretical models for transition metal oxides. There have however been many convenient approaches to the understanding and description of their electronic structures and properties.

The extraordinary range of structures and properties of transition metal oxides makes them worthy of special attention. These oxides provide an excellent case study in solid state chemistry and an appropriate gateway to understanding the behavior of inorganic solids. This monograph provides a rather detailed presentation of structures of various classes of complex transition metal oxides, particularly in polyhedral representation, since an appreciation of the structures is essential to an understanding of the properties and to design synthesis. We have tried to put together succinctly the salient features of transition metal oxides with respect to their properties as well as the phenomena exhibited by them. We have then described some of the important strategies employed for the preparation of oxides. While it is difficult to do

justice to every aspect of transition metal oxides because of limitation of space, the material presented here should provide a fairly comprehensive picture of the present state of the subject. We believe that the book serves to bring out the flavor of modern inorganic solid state chemistry, through the medium of oxides. By making use of standard texts in solid state physics and chemistry for explanations of some of the terms and concepts, where necessary, readers should be able to comprehend the essence of this book. We trust that the book will be found useful by students, teachers, and practitioners of inorganic chemistry and solid state chemistry as well as condensed matter science and materials science.

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## 1 Introduction

The chemistry of transition metal oxides can be understood only when we have a sound knowledge of the crystal chemistry of these materials. Crystal chemistry represents not only the crystal structures of the oxides, but also the nature of bonding in them. Crystal chemistry is indeed a crucial constituent of solid state chemistry and provides the basis for designing and synthesizing new materials (for general review about inorganic crystal chemistry see for instance ref 1 to 9). Transition metal oxides are by far the most fascinating class of materials when it comes to crystal chemistry. Metal oxides crystallize in a variety of structures, and bonding in these materials can vary anywhere from ionic (e.g., MgO, $Fe_{1-x}O$) to metallic (TiO, $ReO_3$). Associated with such changes in bonding, these materials also show a gamut of fascinating properties. In recent years, it has been possible to determine the structures of complex transition metal oxides by employing some of the new techniques of crystallography. Today, we can obtain detailed structures not only of oxides in single crystal form, but also of powders employing methods of X-ray and neutron diffraction. These two techniques have become really powerful because of the availability of synchrotron X-rays and intense pulsed neutron sources.

To fully understand the structures of complex transition metal oxides, it becomes necessary to understand not only the crystal structure and bonding, but also the local or ultramicrostructures, often arising from defects or compositional changes. Local structure of oxides is best studied by high resolution

electron microscopy. In the last two decades, this technique has been employed widely to establish the ultramicrostructures of a large number of complex transition metal oxides. With the availability of commercial electron microscopes of 1.7 Å resolution, it is possible to pinpoint the nature of defects or local ordering in atomistic detail.

In Part I we shall examine the structures of a variety of transition metal oxides and in doing so, we shall describe the structures by means of polyhedral representation. Since it is important to visualize structures to be able to design new oxides of novel structures or to understand the properties of known ones, we discuss in detail the structures of a large number of examples from the different families of transition metal oxides.

Before we go into the various structural families, we shall briefly discuss some elements of crystal chemistry and the notion of defects in crystals. The presence of defects and more precisely, the ordering of defects in transition metal oxides, gives rise to new structural principles such as the crystallographic shear. Structures of transition metal oxides are governed by such principles giving rise to novel features such as homology, superstructures, intergrowths, and tunnels. We shall also briefly discuss some aspects of the techniques of characterization and phase transitions. Clearly, each of these topics—defects, techniques, and phase transitions—is by itself so vast in scope that we can only present the highlights in a rudimentary fashion to provide the necessary background to look at the structures of transition metal oxides.

## 2 Basic Background Material

### 2.1 Description of Crystalline Oxides

Crystals are composed of infinite arrays of atoms, ions, or molecules in the three dimensions. Periodicity in crystals is generally represented by replacing the repeating unit by a point, the resulting array of such points in space being called a lattice. In a *space lattice,* the translation vectors, **a**, **b**, and **c** in the three crystallographic directions define a *primitive cell.* When a primitive cell or some other suitable combination is chosen as the repeating unit of the lattice, it is referred to as the *unit cell.* A crystallographic unit cell is defined by three translation vectors and three angles $\alpha$, $\beta$, and $\gamma$. The seven *crystal systems,* based on the six parameters are cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic, and tetragonal. There are 14 independent ways of arranging points in three dimensions, giving rise to the 14 *Bravais lattices* listed in Table 1 and shown in Figure 1.

Based on extensive studies of the symmetry in crystals, it is found that crystals possess one or more of the 10 basic symmetry elements (five proper rotation axes, 1, 2, 3, 4, 6, and five inversion or improper axes). A set of symmetry elements intersecting at a common point within a crystal is called the *point group.* The 10 basic symmetry elements along with their 22 possible

**Table 1** Crystal Systems and Bravais Lattices

| System | Unit Cell Specification | Essential Symmetry[a] | Bravais Lattice[b] |
|---|---|---|---|
| Cubic | $a = b = c$<br>$\alpha = \beta = \gamma = 90°$ | Four 3*s* | P, I, F |
| Tetragonal | $a = b \neq c$<br>$\alpha = \beta = \gamma = 90°$ | One 4 or $\bar{4}$ | P, I |
| Orthorhombic | $a \neq b \neq c$<br>$\alpha = \beta = \gamma = 90°$ | Three 2*s* mutually perpendicular or one 2 intersecting with two *m*'s | P, I, C, F |
| Rhombohedral | $a = b = c$<br>$\alpha = \beta = \gamma \neq 90°$ | One 3 | R (P) |
| Hexagonal | $a = b \neq c$<br>$\alpha = \beta = 90°$<br>$\gamma = 120°$ | One 6 | P |
| Monoclinic | $a \neq b \neq c$<br>$\alpha = \gamma = 90° \neq \beta$ | One 2 or one *m* | P<br>C |
| Triclinic | $a \neq b \neq c$<br>$\alpha \neq \beta \neq \gamma$ | none | P |

[a] Unmodified numbers (3, 4, etc.) are rotation axes; overbars indicate; inversion axes *m* is mirror plane.
[b] P, Primitive lattice containing lattice points at the corners of the unit cell; F, face-centered lattice; I, body-centered lattice.

combinations constitute the 32 *crystal classes.* Additional symmetry elements in crystals are the *screw axis* and the *glide plane.* A *space group* is a combination of these elements involving translation with the point group symmetry. For example, while there are only two possible space groups, $P1$ and $P\bar{1}$ for a triclinic system, there are 13 possible space groups in a monoclinic system. In all, there are 230 possible space groups.

Based on bonding considerations, five types of crystals can be defined: ionic, covalent, metallic, molecular (van der Waals), and hydrogen-bonded. Ionic crystals are formed between highly electropositive and highly electronegative elements, which favor electron transfer to produce oppositely charged ions, generally with closed-shell electronic configurations. Following Born, the cohesive energy of ionic crystals, $U$, containing oppositely charged ions with charges $Z_1$ and $Z_2$ at a distance $R$, is written as the sum of two terms, one due to attraction and the other due to repulsion:

$$U = \frac{AZ_1Z_2e^2}{R} + B \exp\left(\frac{R}{\rho}\right)$$

Here, the *Madelung constant, A*, is characteristic of the geometric arrangement of ions in crystals, $B$ is the repulsion constant, and $\rho$ the repulsion exponent. The repulsion term accounts for the stability of ionic crystals without collapsing and arises from the ability of ions with closed electron shells to resist overlap of their electron clouds with neighboring ions. The constants $B$ and $\rho$ are respectively a measure of the strength and the range of the repulsive interac-

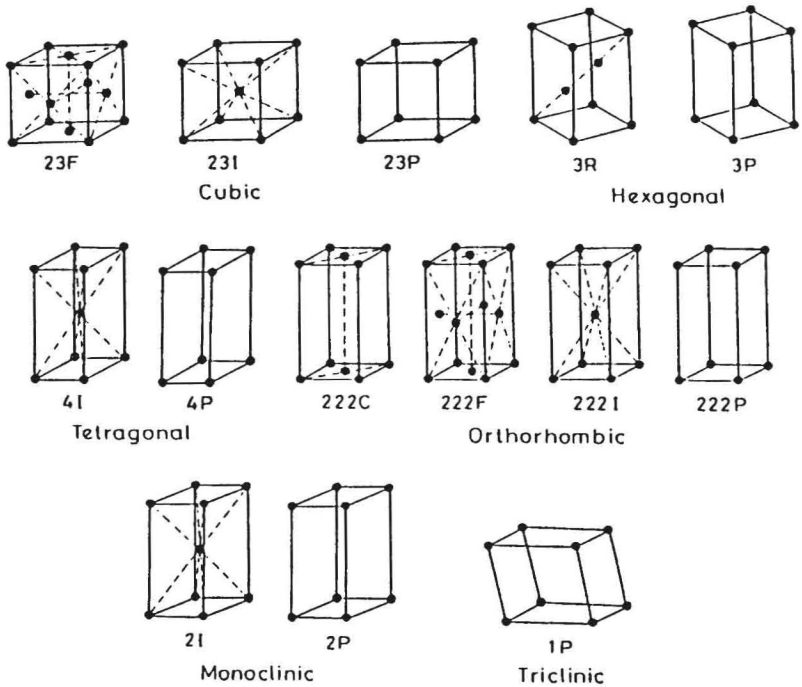


**Figure 1.** Fourteen Bravais lattices: letters P, F, I, and C represent type of lattice; numbers represent the symmetry axes.

tion. The Madelung constant is a function of crystal structure and is computed from the geometrical arrangement of ions in the crystal. For example, the Madelung constant for the NaCl structure has a value of 1.74756. The preceding equation for $U$ is only approximate, and it is necessary to include contributions from van der Waals forces and the correction for zero-point energy. These are, however, minor terms accounting for a small percentage of the total lattice energy. Cohesive energies of ionic solids have been extensively reviewed in the literature.[10,11] Experimental lattice energies of ionic solids are obtained from the *Born–Haber cycle.* The ionic model is a poor approximation for crystals containing large anions and small cations (e.g., oxides and sulfides), where the covalent contribution to bonding becomes significant. Furthermore, cohesive energy calculations cannot be used a priori to predict the structure of an ionic solid, since the method employs experimental interatomic distances in conjunction with formal ionic charges.

Typical covalent solids are formed by group IV elements such as carbon, silicon, and germanium. These elements crystallize in the diamond structure wherein each atom is bonded to four others through covalent bonds. Atoms in covalent solids tend to achieve closed-shell electronic configuration by electron sharing with neighbors. Unlike an ionic bond, a covalent bond has