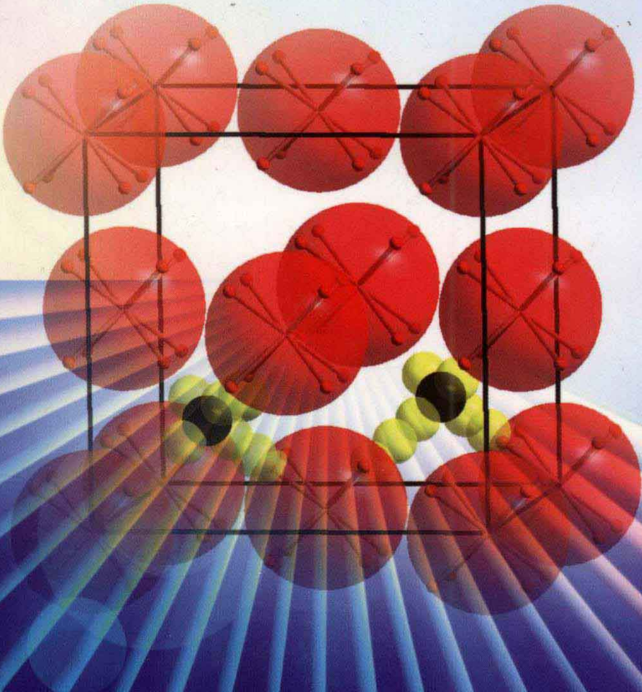
Inorganic Materials Series



Functional Oxides

Editors

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WILEY

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WILEY
A John Wiley and Sons, Ltd, Publication

This edition first published 2010

Registered office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

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Library of Congress Cataloging-in-Publication Data

Functional oxides / edited by Duncan W. Bruce, Dermot O'Hare, Richard I. Walton.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-470-99750-5
1. Organic oxides. 2. Inorganic compounds. I. Bruce, Duncan W. II. O'Hare, Dermot. III. Walton, Richard I.
QD181.O1F87 2010
546′.7212—dc22

2009041495

A catalogue record for this book is available from the British Library.

ISBN: 978-0-470-99750-5 (Cloth)

Set in 10.5/13 Sabon by Integra Software Services Pvt. Ltd, Pondicherry, India.
Printed and bound by TJ International, Padstow, Cornwall

Functional Oxides

Inorganic Materials Series

Series Titles

Functional Oxides
Molecular Materials
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Inorganic Materials Series Preface

Back in 1992, two of us (DWB and DO'H) edited the first edition of *Inorganic Materials* in response to the growing emphasis and interest in materials chemistry. The second edition, which contained updated chapters, appeared in 1996 and was reprinted in paperback. The aim had always been to provide the reader with chapters that, while not necessarily comprehensive, nonetheless gave a first-rate and well-referenced introduction to the subject for the first-time reader. As such, the target audience was from first-year postgraduate student upwards. Authors were carefully selected who were experts in their field and actively researching their topic, so were able to provide an up-to-date review of key aspects of a particular subject, whilst providing some historical perspective. In these two editions, we believe our authors achieved this admirably.

In the intervening years, materials chemistry has grown hugely and now finds itself central to many of the major challenges that face global society. We felt, therefore, that there was a need for more extensive coverage of the area and so Richard Walton joined the team and, with Wiley, we set about a new and larger project. The *Inorganic Materials Series* is the result and our aim is to provide chapters with a similar pedagogical flavour but now with much wider subject coverage. As such, the work will be contained in several themed volumes. Many of the early volumes concentrate on materials derived from continuous inorganic solids, but later volumes will also emphasise molecular and soft matter systems as we aim for a much more comprehensive coverage of the area than was possible with *Inorganic Materials*.

We approached a completely new set of authors for the new project with the same philosophy in choosing actively researching experts, but also with the aim of providing an international perspective, so to reflect the diversity and interdisciplinarity of the now very broad area of inorganic materials chemistry. We are delighted with the calibre of authors who have agreed to write for us and we thank them all for their efforts and cooperation. We believe they have done a splendid job and that their work will make these volumes a valuable reference and teaching resource.

DWB, York
DO'H, Oxford
RIW, Warwick
January 2010

Preface

Metal oxides, particularly those containing one or more transition elements, for many years have been the foundation of solid-state inorganic chemistry. Here, the synthetic skill to manipulate the reactivity of diverse chemical elements, often at extreme temperatures and pressures, went hand-in-hand with developments in structural characterisation, including both spectroscopic and diffraction methods. A very good, and indeed already well-documented example, is the case of the cuprate superconductors, discovered in the early 1980s, which led to increasing complex structural chemistry and which continues to push the frontiers of knowledge of electronic properties of the solid-state. The interplay between the synthetic and structural work of chemists and the property measurement and theory of physicists led to the rapid development in understanding of a unique group of materials. When one also considers the role of the materials scientist in device fabrication of such electronic materials, the area is seen to be truly interdisciplinary.

Oxides continue to be the focus of much attention, and increasingly the area is driven by target properties. In this volume we have been largely concerned with properties arising from electronic structure but other applications, in catalysis or in optical media, are equally as important and are researched equally actively. The role of the chemist in synthesis is still paramount, and indeed it is very apparent that the scope for novel compositions and structures is far from being exhausted. More than ever the goal of a particular desirable property and the need to understand structure–property relationships is always in mind in contemporary research.

A complete review of the field of oxides would probably be impossible in a single volume, so instead we have selected five topical areas of functional oxides that illustrate their importance in modern materials chemistry. These highlight structural chemistry, magnetic properties, electronic properties, ionic conduction but also other emerging areas of importance in energy, such as thermoelectricity.

We approached five leading groups at the cutting edge of research to review these representative areas of functional oxides. We are very pleased that they agreed to write chapters for us, and that they have done such a good job in clearly explaining complex topics in an accessible way. We hope you will agree that these chapters provide an excellent introduction to what is an international field of great breadth.

DWB, York
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Noncentrosymmetric Inorganic Oxide Materials: Synthetic Strategies and Characterisation Techniques

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1.1 INTRODUCTION

Materials that are crystallographically noncentrosymmetric (NCS), or acentric, are of current interest attributable to their functional properties, including piezoelectricity, ferroelectricity, and second-harmonic generation. Numerous relationships occur between these properties and crystal classes.[1] These relationships are shown in Figure 1.1, along with several well-known materials. It is instructive if we examine this figure more closely. If we examine the left-side of Figure 1.1, the symmetry dependent property we encounter is enantiomorphism, and the chiral crystal classes. All chiral materials must crystallise in one of eleven crystal classes, 1 (C_1), 2 (C_2), 3 (C_3), 4 (C_4), 6 (C_6), 222 (D_2), 32 (D_3), 422 (D_4), 622 (D_6), 23 (T), or 432 (O). Materials found in any of these crystal classes have a 'handedness', and a nonsuperimposable mirror image. The well-known

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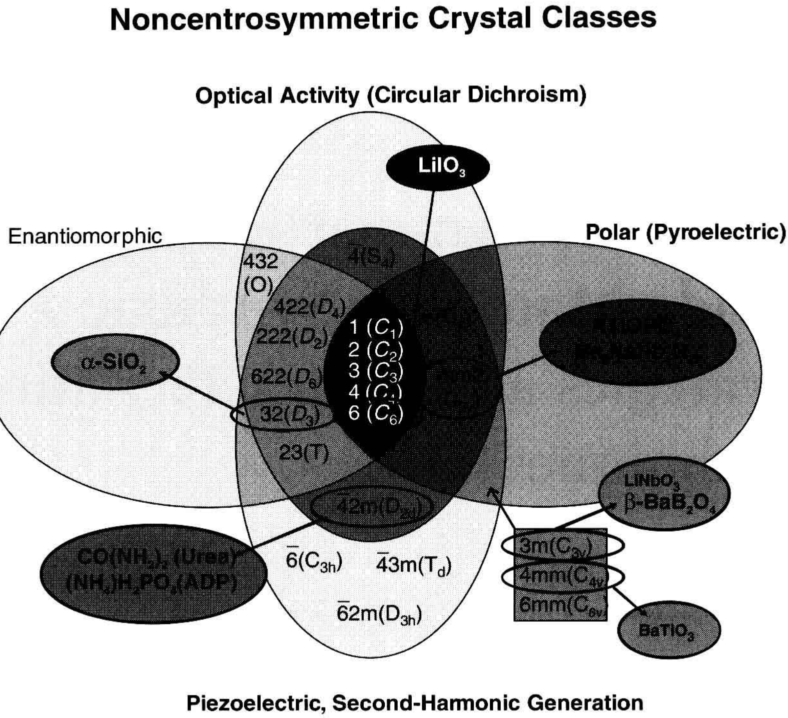

Figure 1.1 The relationships with respect to symmetry-dependent property between the noncentrosymmetric crystal classes are given along with representative compounds. Note that only five crystal classes, 1 (C_1), 2 (C_2), 3 (C_3), 4 (C_4), and 6 (C_6) have the proper symmetry for all of the symmetry dependent properties. Adapted from Halasyamani and Poeppelmeier, 1998 [71]. Copyright 1998 American Chemical Society

chiral material α-SiO_2[2, 3] crystallises in crystal class 32 (D_3). If we examine the right-side of Figure 1.1, we encounter the ten polar crystal classes, 1 (C_1), 2 (C_2), 3 (C_3), 4 (C_4), 6 (C_6), m (C_s), $mm2$ (C_{2v}), $3m$ (C_{3v}), $4mm$ (C_{4v}), and $6mm$ (C_{6v}). Materials found in these crystal classes have a permanent dipole moment. In fact $LiIO_3$,[4, 5] which crystallises in crystal class 6 (C_6) is both chiral and polar. The other materials shown: $KTiOPO_4$ (KTP)[6] and $Ba_2NaNb_5O_{15}$ ($mm2$ for both),[7] $LiNbO_3$ [8, 9] and β-BaB_2O_4 ($3m$ for both),[10, 11] and $BaTiO_3$ ($4mm$) are all 'purely' polar. They all have a dipole moment, but are not chiral. Examples are also given of materials, $CO(NH_2)_2$ (urea)[12] and $(NH_4)H_2PO_4$ (ammonium dihydrogen phosphate, ADP)[13] that crystallise in crystal class $\bar{4}2m$, that are neither chiral nor polar, but are still noncentrosymmetric. Other symmetry-dependent properties that are of importance are second-harmonic generation and piezoelectricity. Except for materials that are found in crystal class 432 (O), all NCS materials exhibit the correct symmetry for second-harmonic generation and piezoelectric behaviour.

Determining if a crystalline material is centrosymmetric or noncentrosymmetric is usually straightforward. From Friedel's law it is known that, during the diffraction process, if the incident wavelength is small compared with the absorption edge of any atom in the crystal, a centre of symmetry is introduced between oppositely related reflections. In other words $I(hkl) = I(-h-k-l)$. Friedel's law fails when the incident wavelength is similar to an atom's absorption edge. This anomalous scattering, when the imaginary part of the scattering factor becomes large, has been exploited to address a host of crystallographic problems.[14] Also, with the diffraction data the intensity distribution between a centric and acentric crystal differs. Statistical indicators of centricity have been developed by Wilson and Howell,[15, 16] but have been shown to be incorrect if the structure contains heavy atoms on special positions. Marsh has emphasised the importance of weak reflections if the centricity is in question.[17, 18] If weak reflections are removed, the statistical distribution tests can be strongly biased toward an acentric indication. Marsh also argues that when the diffraction data do not provide a clear choice between centrosymmetric and noncentrosymmetric space groups the centrosymmetric space group is preferred, even if disorder occurs.[17] The Platon suite of programs, specifically Addsym, can be used on refined structures to check for missing symmetry, *e.g.* inversion centres, as well as mistakes in crystal system or Laue class.[19]

1.2 STRATEGIES TOWARD SYNTHESISING NONCENTROSYMMETRIC INORGANIC MATERIALS

In the past decade or so a number of strategies have been described whose aim was to increase the incidence of acentricity in any new material. In one manner or another, each of these strategies involves crystal engineering.[20] One question that needs to be addressed is why there are so few (relatively) NCS materials? It is estimated that only $\sim$15% of all inorganic materials are NCS. This would indicate that in the vast majority of inorganic materials, the 'building blocks' of the structure are centrosymmetric, *i.e.* made up of regular polyhedra. These regular polyhedra are usually related