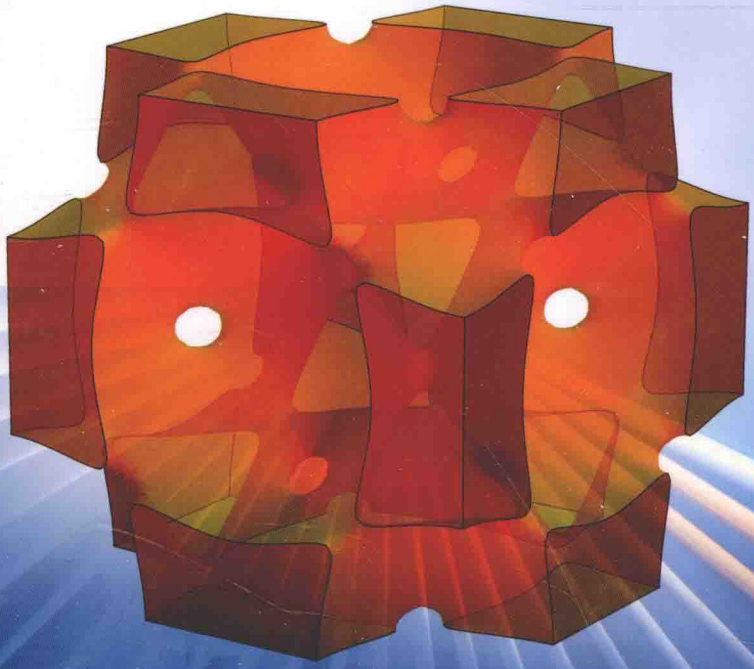
Inorganic Materials Series



Structure from Diffraction Methods

Editors
Duncan W. Bruce | Dermot O'Hare | Richard I. Walton

WILEY

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This edition first published 2014

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

Library of Congress Cataloging-in-Publication Data applied for.

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

ISBN: 9781119953227

Set in 10.5/13pt Sabon by Laserwords Private Limited, Chennai, India
Printed and bound in Malaysia by Vivar Printing Sdn Bhd

1 2014

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Series Titles

Functional Oxides
Molecular Materials
Porous Materials
Low-Dimensional Solids
Energy Materials
Local Structural Characterisation
Multi Length-Scale Characterisation
Structure from Diffraction Methods

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

Preface

Inorganic materials show a diverse range of important properties that are desirable for many contemporary, real-world applications. Good examples include recyclable battery cathode materials for energy storage and transport, porous solids for capture and storage of gases and molecular complexes for use in electronic devices. Some of these families of materials, and many others, were reviewed in earlier volumes of the *Inorganic Materials Series*. When considering the property-driven research in this large field, it is immediately apparent that methods for structural characterisation must be applied routinely in order to understand the function of materials so that their behaviour can be optimised for real applications. Thus 'structure–property relationships' are an important part of research in this area. In order to determine structure effectively, advances in methodology are important: the aim is often rapidly to examine increasingly complex materials so as to gain knowledge of structure over length scales ranging from local atomic order, through crystalline long-range order to the meso- and macroscopic scales.

No single technique can examine all levels of structural order simultaneously and the chapters presented in this volume deal with recent advances in the key techniques that allow investigation of the structure of inorganic materials that are ordered over distances significantly greater than atomic length scales, *i.e.* crystalline materials. Crystalline materials are substances built from regularly repeating 'structural motifs', which may be atoms, ions or molecules, either individually or as groups. All crystals have a defined 'unit cell' that is repeated to form a translationally invariant tiling of space.

Most of the techniques employed to study the identity of the crystal unit cell and its three-dimensional periodicity are based on the elastic scattering of radiation from the material. However, tuning of the wavelength of the scattered radiation allows the periodic order to be probed in subtly different ways and over a range of length scales. So although some of the diffraction methods discussed in this volume may be familiar to the reader (such as single-crystal and powder diffraction), recent advances have both broadened their applicability (*e.g.* study of much smaller single crystals is now possible, and *ab initio* structure solution is feasible from

polycrystalline powder) and made them available more routinely. It is therefore timely to provide up-to-date overviews of their use.

Also included are techniques that can probe the details of the three-dimensional arrangements of atoms in nanocrystalline solids, which allow aspects of disorder in otherwise crystalline materials to be studied. Electron diffraction and total scattering techniques have thus developed so rapidly in recent years that separate chapters on these techniques are warranted. Small-angle scattering is a technique we were keen to include as it is often overlooked as one that can probe the ordered structure of materials below the length scale of powder diffraction methods.

We approached an international set of expert authors to write the chapters in this volume with the brief to provide an introduction to the principles of their technique, to describe recent developments in the field and then to select examples from the literature to illustrate the method under discussion. We believe they have done an excellent job in all respects and hope that the chapters provide a valuable set of references for those who wish to learn the principles of contemporary diffraction methods in the study of Inorganic Materials.

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September 2013

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Powder Diffraction

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1.1 INTRODUCTION

As discussed in Chapter 2, **single-crystal X-ray diffraction**[1–3] **(XRD)** is the most widely used and the most powerful technique for determining crystal structures, and this technique led to many monumental scientific discoveries in the 20th century. The wide-ranging scope and the routine application of single-crystal XRD in the modern day have arisen both through advances in instrumentation and through the development of powerful strategies for data analysis, such that crystal structures can now be determined rapidly and straightforwardly in all but the most challenging cases. The central importance of single-crystal XRD in the physical, biological and materials sciences will continue to be further developed and exploited in the years to come. Thus, provided a single crystal of sufficient size and quality is available for the material of interest, successful structure determination by analysis of single-crystal XRD data is nowadays very routine.

However, the requirement to prepare a suitable single crystal specimen for single-crystal XRD experiments represents a major limitation of this technique. As a consequence, the crystal structures of many important crystalline materials remain unknown simply because the material cannot be prepared as a crystal of appropriate size and quality for single-crystal XRD studies. In such cases, however, the material can usually be prepared as a microcrystalline powder, and therefore it is still

Structure from Diffraction Methods, First Edition. Edited by Duncan W. Bruce, Dermot O'Hare and Richard I. Walton.