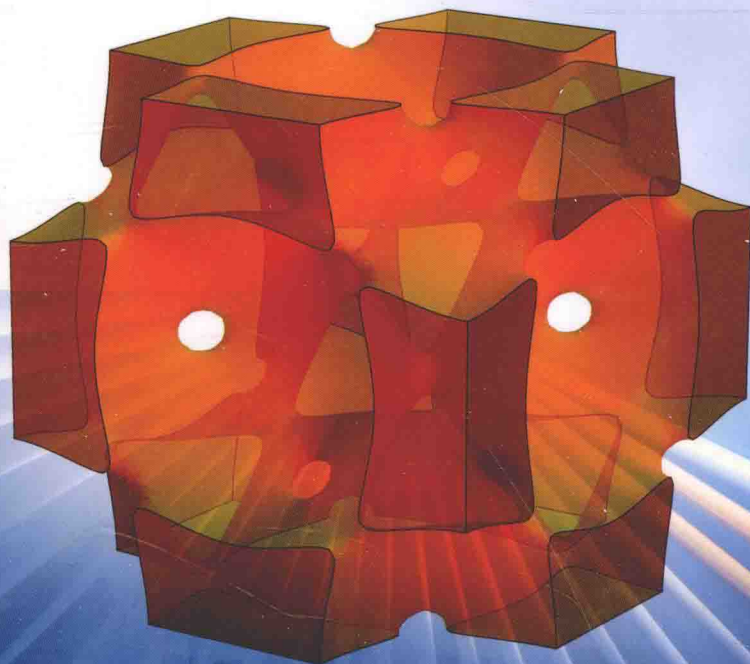


Inorganic Materials Series



Structure from Diffraction Methods

Editors

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

WILEY

Structure from Diffraction Methods

Edited by

Duncan W. Bruce
University of York, UK

Dermot O'Hare
University of Oxford, UK

Richard I. Walton
University of Warwick, UK



WILEY

This edition first published 2014
© 2014 John Wiley & Sons, Ltd

Registered office

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

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. It is sold on the understanding that the publisher is not engaged in rendering professional services and neither the publisher nor the author shall be liable for damages arising herefrom. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or Website is referred to in this work as a citation and/or a potential source of further information does not mean that the author or the publisher endorses the information the organization or Website may provide or recommendations it may make. Further, readers should be aware that Internet Websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the publisher nor the author shall be liable for any damages arising herefrom.

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

Structure from Diffraction Methods

Inorganic Materials Series

Series Editors:

Professor Duncan W. Bruce

Department of Chemistry, University of York, UK

Professor Dermot O'Hare

Chemistry Research Laboratory, University of Oxford, UK

Professor Richard I. Walton

Department of Chemistry, University of Warwick, UK

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.

*DWB, York
DO'H, Oxford
RIW, Warwick
September 2013*

List of Contributors

William Clegg School of Chemistry, Newcastle University, Newcastle upon Tyne, UK

Lu Han School of Chemistry and Chemical Technology, State Key Laboratory of Composite Materials, Shanghai Jiao Tong University, Shanghai, China

Kenneth D. M. Harris School of Chemistry, Cardiff University, Cardiff, UK

Keiichi Miyasaka Graduate School of EEWS, WCU Energy Science & Engineering, KAIST, Daejeon, Republic of Korea; Department of Applied Quantum Physics and Nuclear Engineering, Graduate School of Engineering, Kyusyu University, Fukuoka, Japan

Theyencheri Narayanan European Synchrotron Radiation Facility, Grenoble, France

Reinhard B. Neder Crystallography, Department of Physics, University of Erlangen, Erlangen, Germany

Osamu Terasaki Graduate School of EEWS, WCU Energy Science & Engineering, KAIST, Daejeon, Republic of Korea; Department of Materials & Environmental Chemistry, EXSELENT, Stockholm University, Stockholm, Sweden

P. Andrew Williams School of Chemistry, Cardiff University, Cardiff, UK

Contents

<i>Inorganic Materials Series Preface</i>	<i>xi</i>
<i>Preface</i>	<i>xiii</i>
<i>List of Contributors</i>	<i>xv</i>
1 Powder Diffraction	1
<i>Kenneth D. M. Harris and P. Andrew Williams</i>	
1.1 Introduction	1
1.2 The Similarities and Differences between Single-Crystal XRD and Powder XRD	2
1.3 Qualitative Aspects of Powder XRD: 'Fingerprinting' of Crystalline Phases	6
1.4 Quantitative Aspects of Powder XRD: Some Preliminaries Relevant to Crystal Structure Determination	8
1.4.1 Relationship between a Crystal Structure and its Diffraction Pattern	8
1.4.2 Comparison of Experimental and Calculated Powder XRD Patterns	10
1.5 Structure Determination from Powder XRD Data	12
1.5.1 Overview	12
1.5.2 Unit Cell Determination (Indexing)	14
1.5.3 Preparing the Intensity Data for Structure Solution: Profile Fitting	15
1.5.4 Structure Solution	16
1.5.5 Structure Refinement	21
1.6 Some Experimental Considerations in Powder XRD	22
1.6.1 Synchrotron <i>versus</i> Laboratory Powder XRD Data	22
1.6.2 Preferred Orientation	24
1.6.3 Phase Purity of the Powder Sample	25
1.6.4 Analysis of Peak Widths in Powder XRD Data	26
1.6.5 Applications of Powder XRD for <i>In Situ</i> Studies of Structural Transformations and Chemical Processes	28

1.7	Powder Neutron Diffraction <i>versus</i> Powder XRD	30
1.8	Validation of Procedures and Results in Structure Determination from Powder XRD Data	33
1.8.1	Overview	33
1.8.2	Validation before Direct-Space Structure Solution	34
1.8.3	Aspects of Validation following Structure Refinement	36
1.9	More Detailed Consideration of the Application of Powder XRD as a 'Fingerprint' of Crystalline Phases	40
1.10	Examples of the Application of Powder XRD in Chemical Contexts	44
1.10.1	Overview	44
1.10.2	Structure Determination of Zeolites and Other Framework Materials	45
1.10.3	<i>In Situ</i> Powder XRD Studies of Materials Synthesis	47
1.10.4	Structure Determination of New Materials Produced by Solid-State Mechanochemistry	49
1.10.5	<i>In Situ</i> Powder XRD Studies of Solid-State Mechanochemical Processes	52
1.10.6	<i>In Situ</i> Powder XRD Studies of a Polymorphic Transformation	54
1.10.7	<i>In Situ</i> Powder XRD Studies of a Solid-State Reaction	57
1.10.8	Establishing Details of a Hydrogen-Bonding Arrangement by Powder Neutron Diffraction	57
1.10.9	Structure Determination of a Material Produced by Rapid Precipitation from Solution	59
1.10.10	Structure Determination of Intermediates in a Solid-State Reaction	61
1.10.11	Structure Determination of a Novel Aluminium Methylphosphonate	61
1.10.12	Structure Determination of Materials Prepared by Solid-State Dehydration/Desolvation Processes	62
1.10.13	Structure Determination of the Product Material from a Solid-State Photopolymerisation Reaction	65
1.10.14	Exploiting Anisotropic Thermal Expansion in Structure Determination	67

1.10.15	Rationalisation of a Solid-State Reaction	68
1.10.16	Structure Determination of Organometallic Complexes	70
1.10.17	Examples of Structure Determination of Some Polymeric Materials	71
1.10.18	Structure Determination of Pigment Materials	72
1.11	Concluding Remarks	73
	References	74
2	X-Ray and Neutron Single-Crystal Diffraction	83
	<i>William Clegg</i>	
2.1	Introduction	83
2.2	Solid-State Fundamentals	86
2.2.1	Translation Symmetry	87
2.2.2	Other Symmetry	91
2.2.3	An Introduction to Non-Ideal Behaviour	98
2.3	Scattering and Diffraction	101
2.3.1	Fundamentals of Radiation and Scattering	102
2.3.2	Diffraction of Monochromatic X-Rays	103
2.3.3	Diffraction of Polychromatic X-Rays	110
2.3.4	Diffraction of Neutrons	111
2.3.5	Some Competing and Complicating Effects	114
2.4	Experimental Methods	119
2.4.1	Radiation Sources	119
2.4.2	Single Crystals	124
2.4.3	Measuring the Diffraction Pattern	126
2.4.4	Correcting for Systematic Errors	127
2.5	Structure Solution	128
2.5.1	Direct Methods	130
2.5.2	Patterson Synthesis	131
2.5.3	Symmetry Arguments	132
2.5.4	Charge Flipping	133
2.5.5	Completing a Partial Structure Model	134
2.6	Structure Refinement	138
2.6.1	Minimisation and Weights	139
2.6.2	Parameters, Constraints and Restraints	139
2.6.3	Refinement Results	140
2.6.4	Computer Programs for Structure Solution and Refinement	141

2.7	Problem Structures, Special Topics, Validation and Interpretation	142
2.7.1	Disorder	142
2.7.2	Twinning	143
2.7.3	Pseudosymmetry, Superstructures and Incommensurate Structures	145
2.7.4	Absolute Structure	147
2.7.5	Distinguishing Element Types, Oxidation States and Spin States	148
2.7.6	Valence Effects	149
2.7.7	Diffraction Experiments under Non-Ambient Conditions	150
2.7.8	Issues of Interpretation and Validation	151
	Software Acknowledgements	153
	References	153
3	PDF Analysis of Nanoparticles	155
	<i>Reinhard B. Neder</i>	
3.1	Introduction	155
3.2	Pair Distribution Function	160
3.3	Data Collection Strategies	168
3.4	Data Treatment	170
3.4.1	Calculation of $G(r)$ from a Structural Model	175
3.4.2	Data Modelling	183
3.5	Examples	184
3.5.1	Local Disorder <i>versus</i> Long-Range Average Order	185
3.5.2	ZnSe Nanoparticle	189
3.5.3	Decorated ZnO Nanoparticle	194
3.6	Complementary Techniques	197
	References	199
4	Electron Crystallography	201
	<i>Lu Han, Keiichi Miyasaka and Osamu Terasaki</i>	
4.1	Introduction	201
4.2	Crystal Description	203
4.2.1	Fourier Transformation and Related Functions	203
4.2.2	Lattices	204

4.2.3	Crystals and Crystal Structure Factors	205
4.2.4	Simple Description of Babinet's Principle	206
4.3	Electron Microscopy	208
4.3.1	Interaction between Electrons and Matter	208
4.3.2	Scanning Electron Microscopy	209
4.3.3	Transmission Electron Microscopy	214
4.4	Electron Diffraction	216
4.4.1	X-Rays (Photons) <i>versus</i> Electrons	216
4.4.2	Scattering Power of an Atom	217
4.4.3	Crystal Structure and Electron Diffraction	219
4.4.4	Relationship between Real and Reciprocal Space	221
4.4.5	Friedel's Law and Phase Restriction	223
4.4.6	Information on the 0th, 1st and Higher-Order Laue Zone	224
4.4.7	Determining Unit Cell Dimensions and Crystal Symmetry	226
4.4.8	Convergent Beam Electron Diffraction	227
4.5	Imaging	229
4.5.1	Crystal Structure and TEM Images	229
4.5.2	Image Resolution	230
4.5.3	Limitation of Structural Resolution	231
4.5.4	Electrostatic Potential and Structure Factors	232
4.5.5	Image Simulation	235
4.6	The EC Method of Solving Crystal Structures	235
4.6.1	1D Structures	236
4.6.2	2D Structures	239
4.6.3	3D Structures	240
4.7	Other TEM Techniques	249
4.7.1	STEM and HAADF	249
4.7.2	Electron Tomography	249
4.7.3	3D Electron Diffraction	252
4.8	Conclusion	254
	Acknowledgment	256
	References	256
5	Small-Angle Scattering	259
	<i>Theyencheri Narayanan</i>	
5.1	Introduction	259
5.2	General Principles of SAS	261

5.2.1	Momentum Transfer	261
5.2.2	Differential Scattering Cross-Section	262
5.2.3	Non-Interacting Systems	264
5.2.4	Influence of Polydispersity	266
5.2.5	Asymptotic Forms of $I(q)$	268
5.2.6	Multilevel Structures	269
5.2.7	Non-Particulate Systems	272
5.2.8	Structure Factor of Interactions	273
5.2.9	Highly Ordered Structures	275
5.3	Instrumental Set-Up for SAXS	279
5.3.1	Synchrotron Source	280
5.3.2	X-Ray Optics	281
5.3.3	X-Ray Detectors	283
5.3.4	SAXS Instrument Layout	284
5.4	Instrumental Set-Up for SANS	285
5.4.1	Neutron Sources	286
5.4.2	Neutron Optics	287
5.4.3	Neutron Detectors	288
5.4.4	SANS Instrument Layout	289
5.5	Additional Requirements for SAS	290
5.5.1	Combination with Wide-Angle Scattering	290
5.5.2	Instrumental Smearing Effects	292
5.5.3	Sample Environments	293
5.6	Application of SAS Methods	294
5.6.1	Real-Time and <i>In Situ</i> Studies	295
5.6.2	Ultra Small-Angle Scattering	303
5.6.3	Contrast Variation in SAS	308
5.6.4	Grazing-Incidence SAS	314
5.7	Conclusion	318
	Acknowledgements	318
	References	319
	<i>Index</i>	325

1

Powder Diffraction

Kenneth D. M. Harris and P. Andrew Williams

School of Chemistry, Cardiff University, Cardiff, UK

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.

© 2014 John Wiley & Sons, Ltd. Published 2014 by John Wiley & Sons, Ltd.