Inorganic Materials Series



# Structure from Diffraction Methods

Editors

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

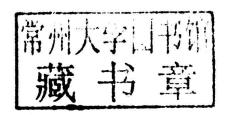
# Structure from Diffraction Methods

Edited by

Duncan W. Bruce University of York, UK

Dermot O'Hare University of Oxford, UK

Richard I. Walton University of Warwick, UK





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

## 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

xiv PREFACE

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

In	organ	ic Mater	rials Series Preface	$x_i$
Pı	reface			xiii
Li	ist of (	Contribi	utors	xv
1	Powder Diffraction Kenneth D. M. Harris and P. Andrew Williams			1
	1.1	Introd	uction	1
	1.2		milarities and Differences between Single-Crystal and Powder XRD	2
	1.3	-	ative Aspects of Powder XRD: 'Fingerprinting' stalline Phases	6
	1.4		itative Aspects of Powder XRD: Some inaries 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	Structu	are Determination from Powder XRD Data	12
		1.5.1	Overview	12
		1.5.2	Unit Cell Determination (Indexing)	14
		1.5.3		
			Solution: Profile Fitting	15
		1.5.4	Structure Solution	16
		1.5.5	Structure Refinement	21
	1.6	Some I	Experimental Considerations in Powder XRD	22
		1.6.1	Synchrotron versus 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

vi CONTENTS

1.7	Powder	Neutron Diffraction versus Powder XRD	30
1.8	Validati	on of Procedures and Results in Structure	
	Determi	nation 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 D	etailed Consideration of the Application	
	of Powd	ler XRD as a 'Fingerprint' of Crystalline Phases	40
1.10		es of the Application of Powder XRD in Chemical	
	Context	* *	44
	1.10.1	Overview	44
	1.10.2	Structure Determination of Zeolites and Other	
		Framework Materials	45
	1.10.3	In Situ Powder XRD Studies of Materials	
		Synthesis	47
	1.10.4	Structure Determination of New Materials	
		Produced by Solid-State Mechanochemistry	49
	1.10.5	In Situ Powder XRD Studies of Solid-State	
		Mechanochemical Processes	52
	1.10.6	In Situ Powder XRD Studies of a Polymorphic	
		Transformation	54
	1.10.7	In Situ 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

CONTENTS	vii

			5 Rationalisation of a Solid-State Reaction 6 Structure Determination of Organometallic	68
		1.10.10	Complexes	70
		1.10.1	7 Examples of Structure Determination	70
		1.10.1	of Some Polymeric Materials	71
		1.10.18	8 Structure Determination of Pigment Materials	72
	1.11		iding Remarks	73
		rences		74
2	X-Ray and Neutron Single-Crystal Diffraction			83
		iam Cleg		03
	2.1	2.1 Introduction		
	2.2	Solid-S	tate Fundamentals	83 86
		2.2.1	Translation Symmetry	87
		2.2.2		91
		2.2.3		98
	2.3	Scatter	ing and Diffraction	101
		2.3.1		102
		2.3.2		103
		2.3.3		110
		2.3.4	Diffraction of Neutrons	111
		2.3.5	Some Competing and Complicating Effects	114
	2.4	Experir	mental 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	Structu	re 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		re 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

viii CONTENTS

	2.7	Proble	m Structures, Special Topics, Validation	
			terpretation	142
		2.7.1		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
	Softv	ware Acl	knowledgements	153
	Refe	rences		153
3	PDF	Analysis	s of Nanoparticles	155
	Reinhard B. Neder			
	3.1	Introdu	uction	155
	3.2	Pair Di	istribution Function	160
	3.3		Collection Strategies	168
	3.4	Data T	reatment	170
		3.4.1	Calculation of $G(r)$ from a Structural Model	175
		3.4.2	8	183
	3.5	Examp		184
		3.5.1	Local Disorder versus Long-Range	
			Average Order	185
			ZnSe Nanoparticle	189
		3.5.3	1	194
	3.6		ementary Techniques	197
	Refe	rences		199
4	Electron Crystallography			201
	Lu F	lan, Keii	ichi Miyasaka and Osamu Terasaki	
	4.1	Introdu		201
	4.2		Description	203
		4.2.1	Fourier Transformation and Related	
			Functions	203
		422	Lattices	204

CONTENTS

		4.2.3	Crystals and Crystal Structure Factors	205
		4.2.4	Simple Description of Babinet's Principle	206
	4.3			
		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	Electro	on Diffraction	216
		4.4.1	X-Rays (Photons) versus 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	<b>Determining Unit Cell Dimensions</b>	
			and Crystal Symmetry	226
		4.4.8	Convergent Beam Electron Diffraction	227
	4.5	Imagin	g	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	C 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	252 254
	4.8			
		owledge	ment	256
	Refer	rences		256
5	0			259
	Theyencheri Narayanan			
	5.1	Introdu	uction	259
	5.2	Genera	al Principles of SAS	261

x CONTENTS

	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			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	Instrur	mental 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	Additio	onal 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		
	5.6.1	Real-Time and In Situ 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			
Acknowledgements			318
Refe	rences		319
Inde	2x		325