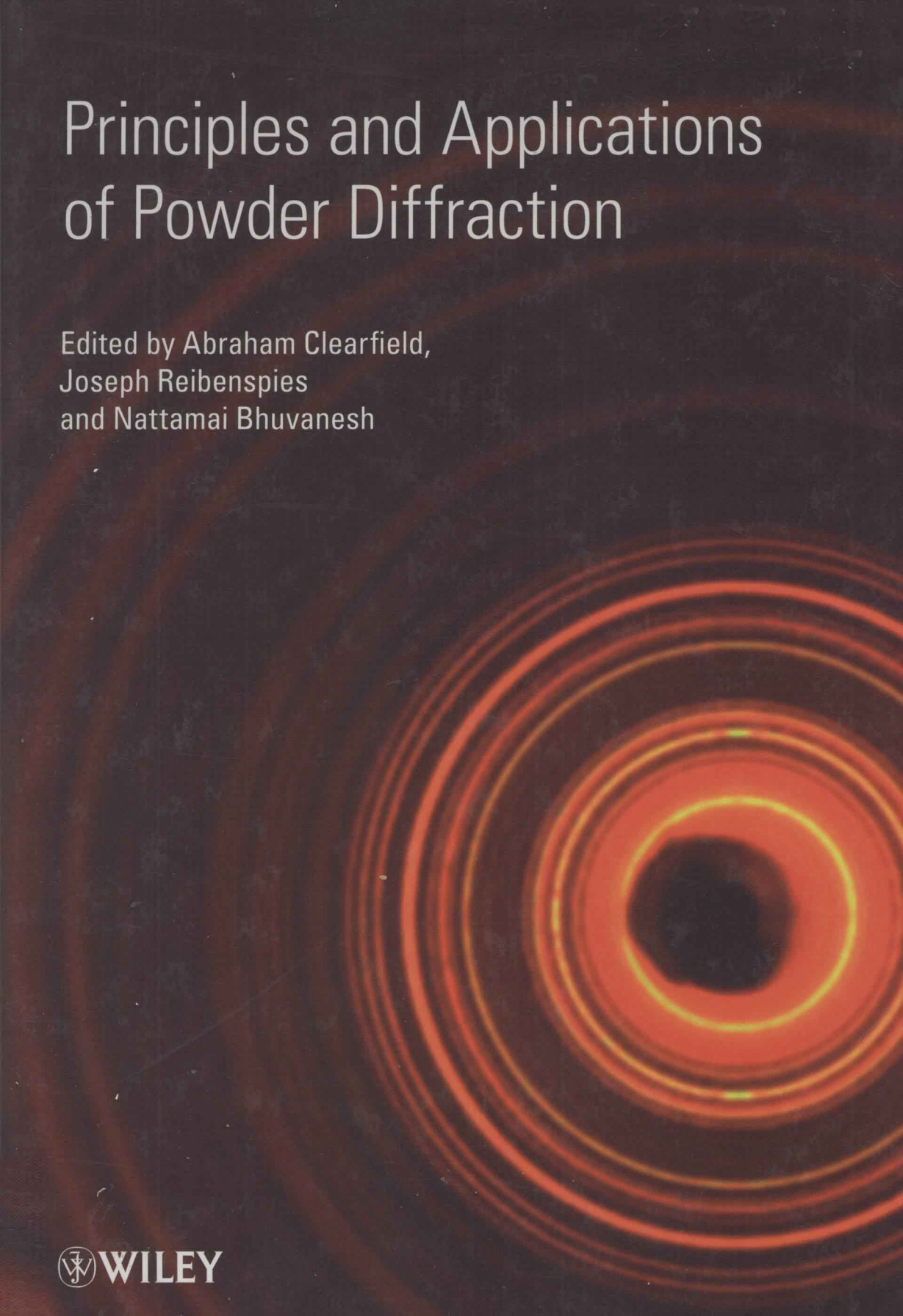
Principles and Applications of Powder Diffraction

Edited by Abraham Clearfield,
Joseph Reibenspies
and Nattamai Bhuvanesh



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Principles and Applications of Powder Diffraction

Dedication

As the saying goes, we all stand on the shoulders of the giants who preceded us.

I, Abraham Clearfield, remember the first lecture I heard where Linus Pauling described the structure of silicates and how it would be possible to understand life processes through solving the structures of biological molecules. I then had the good luck of working with one of Pauling's students, Philip A. Vaugan, for my doctorate. We learned our crystallography from books by Martin J. Buerger and solved structures using Patterson's method. I had the good fortune to hear the first presentation of Hauptman and Karle's direct methods at the ACA meeting held at the University of Michigan. To these and other leaders in the field I am grateful. Of course I would be remiss to not similarly dedicate this book to my wife Ruth who urged me to go on to earn a PhD and has always been my advisor and steadfast supporter.

I, Joseph H. Reibenspies, wish to dedicate this book to my parents, John and Claire, who gave me life and taught me to love learning. I also dedicate this book to my advisor and friend Oren Anderson, who taught me to love science. Finally I dedicate this book to my wife Lisa, who taught me the meaning of love and will always be the love of my life.

I, Nattamai Bhuvanesh, would like to dedicate this book to my parents, my brothers, my wife and kids, my teachers, and to all those who presented me with interesting challenges in science.

Preface

Powder diffraction has been the staple analytical tool for chemists and materials scientists for more than 50 years. Powder diffraction is a tool to identify and characterize materials by analyzing the radiation scattering produced when the materials are illuminated with X-rays or neutrons. The patterns formed by the scattered radiation provide an abundance of information from simple fingerprinting to complex structural analysis. This work will introduce the reader to the world of powder diffraction, why it works and how it works and in the end what you can and cannot do with it. Some of the top researchers in the field of powder diffraction have collaborated on this work to bring the reader the most comprehensive source on the subject. The following paragraphs describe some of the information the reader may find in this work as well as a guide to how to best use the material that is presented.

Chapter 1 contains a short overview of the information obtainable using modern powder diffraction methods to stimulate the reader's interest. The main topics of later chapters (phase identification, structure solution, Rietveld refinement and non-ambient methods) will be introduced in outline using examples from the world of pharmaceuticals, organic and inorganic materials. The limitations of powder diffraction will be detailed as well as comparisons to single-crystal diffraction methods.

Chapter 2 contains all the theory required to understand later chapters and is written at a level suitable for readers following or with an undergraduate science degree. The basic phenomenon of diffraction from a periodic array leading to Bragg's law is developed. The more rigorous derivation of the Laue equations and their visualization via the Ewald sphere will then be introduced to help "demystify" the concept of the reciprocal lattice and its use in crystallography. The chapter describes the basic elements of symmetry and space groups in the solid state and the use of International Tables in powder diffraction problems.

Chapter 3 contains the practical information needed to perform successful powder diffraction measurements using laboratory, synchrotron and neutron sources. The generation of X-rays by typical laboratory sources such as sealed tubes and rotating anodes is discussed. Modern X-ray detectors including scintillation, solid-state, linear position-sensitive detectors and area detectors are highlighted. The general X-ray diffraction experimental setups, such as the Bragg–Brentano and transmission geometry which are of utmost importance is discussed. Focused, para-focusing and pinhole X-ray beams and their applications to normal and micro-diffraction is included. Sample mounting and measuring procedures are described.

Chapter 4 discusses the general area of powder diffraction profile analysis, which includes factors, which affect peak intensity, position and shape. The resolution of the profiles along with a discussion of the various profile analysis functions, including the fundamental parameters approach are explained.

Chapter 5 introduces the reader to "non-laboratory" radiation sources. The chapter highlights the advantages of high brilliance synchrotron X-ray sources. A brief description of the state-of-the-art neutron instrumentation winds up the chapter and finally a discussion on the general uses of neutron powder diffraction concludes the chapter.

Chapter 6 describes some of the "classical" applications of powder X-ray diffraction to sample identification and determination of phase mixtures. Specialized fields such as high-throughput screening and combinatorial analysis are discussed. The use of whole profile analysis, including cell refinement and indices assignment is integrated with search-match methodology. Finally, an overview of the methods for quantitative analysis of crystalline and amorphous containing phases is given.

Chapter 7 describes the topics of structure solution from powder diffraction data. Each stage of the structure solution process is described using examples from both organic and inorganic systems. Both the potential power of the method and its inherent limitations are described. Particular examples of combined neutron and X-ray analysis are highlighted.

Chapter 8 covers topics on Rietveld refinement from powder diffraction data. Each stage of the refinement process is described using examples from both organic and inorganic systems. Both the potential power of the method and its inherent limitations are presented. Particular examples of combined neutron and X-ray analysis will be highlighted. Quantitative analysis by the Rietveld method is outlined.

Chapter 9 presents a number of more specialized/advanced topics not considered in detail elsewhere in the book. These include methods for size/strain analysis using powder diffraction, methods that have become more widely used in nano-technologies and non-ambient methods for studying materials as a function of temperature, pressure, humidity or chemical environment; *in situ* methods for studying phase transitions or chemical reactions by powder diffraction; and the opportunities for structural insight given by pair distribution function analysis.

The editors trust that the reader will find in this book, the elements of X-ray and neutron powder diffraction that are relevant to his or her particular needs.

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Contents

Chapter 1
An Overview of Powder Diffraction

Lachlan M.D. Cranswick

1.1 Introduction

1.1.1 Paths of most resistance and paths of least resistance in pure and applied science

Much of the practicalities of scientific research, and the applied use of science, is in finding the most appropriate paths to reach a desired endpoint (Figure 1.1). The required judgment to discover and differentiate the paths and solutions in a timely manner that lead to a successful research program or industrial initiative can be quite subtle and extensive. Cliffs and walls are many, clear pathways few; constrained by "*good, quick, cheap – pick any two.*" Thus, the aim of this text is to provide the reader with insight on where powder diffraction might provide possible pathways to assist the materials scientist: pathways rocky and smooth, cheaper and more expensive, quick, or on icy routes where haste is best made slowly. Every technique has inconvenient details and pitfalls. So that an inaccurate optimism or inappropriate gloss does not occur, pitfalls and limitations are emphasized in the text.

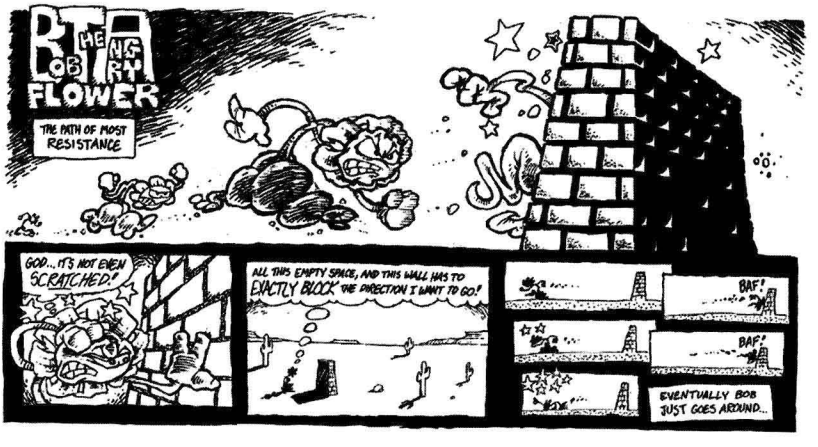

Figure 1.1 "The path of most resistance." (Image courtesy of Stephen Notley, creator of Bob the Angry Flower, http://www.angryflower.com/.)

1.1.2 The usefulness of powder diffraction to materials science

Depending on the intricacies within a program of research, or the requirements of an industrial process, a materials researcher will require access to a variety of scientific techniques. Each technique will have varying degrees of usefulness and importance depending on the research's requirements. Each technique will require a suitable knowledge, learning and expertise to operate at dexterity commensurate with the difficulty of the scientific objectives. Each technique has the potential to provide useful pathways to help reach a successful conclusion.

A major emphasis of materials science is in understanding the elemental compositions and corresponding atomic structures present in materials of interest. This knowledge confirms a material's purity and suitability for use, and allows explanation for its properties and performance. Just as chemical elements form a plethora of compounds, so a compound may pack in different arrays to form a variety of distinct crystal structures (known as polymorphs or phases). An example is carbon, which forms a variety of phases, where the two most commonly known phases are graphite and diamond (Figure 1.2). Elemental composition and physical characteristics such as color and hardness might differentiate phases when encountered in pure form. When in mixtures or reacted with other materials, identification of phases based on physical characteristics or elemental composition can quickly become impossible.

Powder X-ray diffraction (PXRD) offers a convenient method to characterize materials via their constituent crystal structures. When a crystal containing regular repeating arrays of atoms is irradiated by a monochromated X-ray beam, it generates a unique fingerprint in the form of diffraction peaks. By this diffraction process, a powder diffractogram is used to identify crystalline components of a sample. Figure 1.3 shows an example where powder diffraction can easily and unambiguously identify the two crystalline forms of titanium

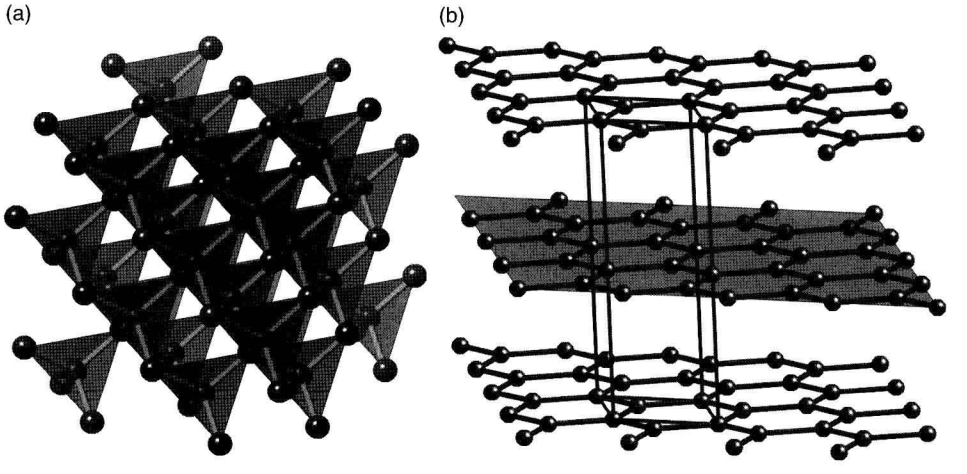

Figure 1.2 Crystal structures for two phases of carbon, (a) diamond with polyhedra showing the 3D tetrahedral co-ordination of the carbon and (b) graphite with unit cell displayed and a plane highlighting the 2D sheets of carbon. (Crystal structures drawn by Ian Swainson using the CrystalMaker software.)

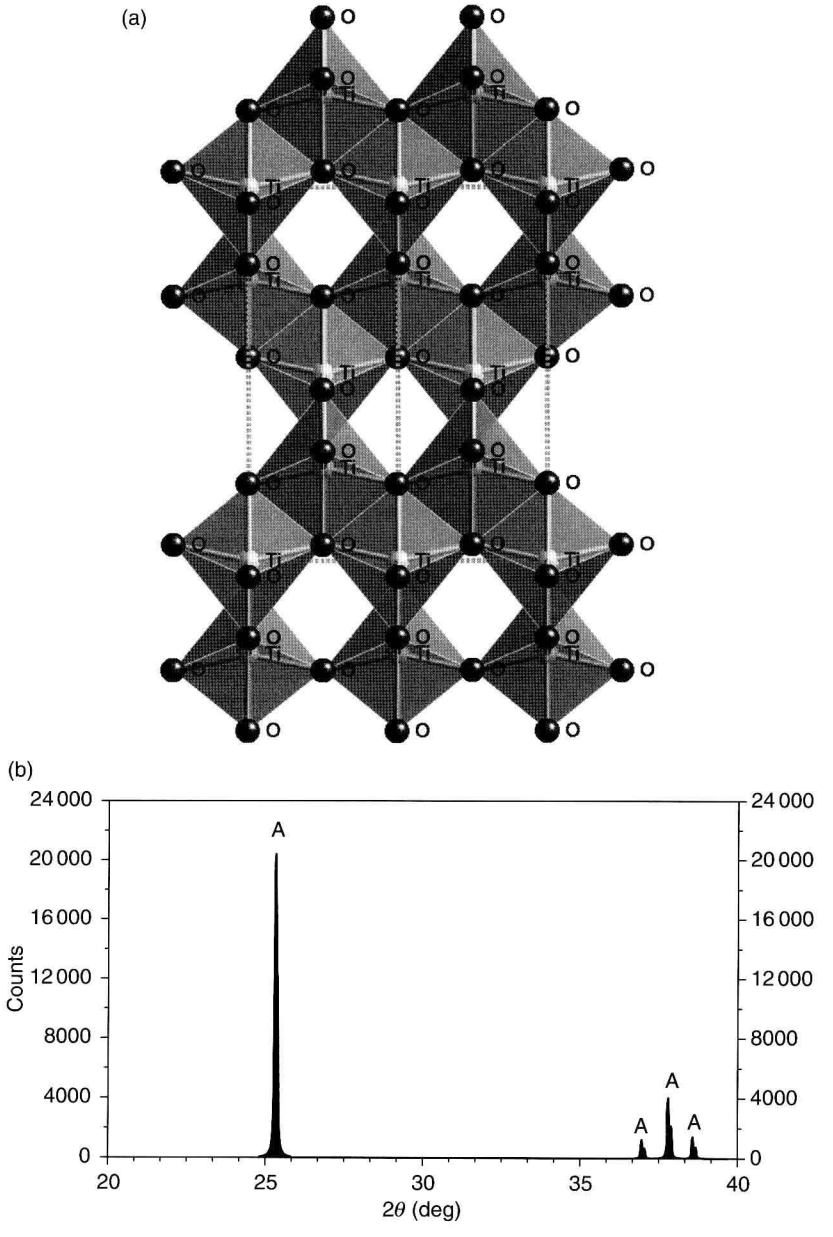

Figure 1.3 (a) Crystal structure of anatase (TiO_2) with unit cell shown using dotted lines, (b) corresponding simulated powder X-ray diffractogram of anatase at Cu X-rays wavelength (1.54056 Å), (c) crystal structure of rutile (TiO_2) with unit cell shown using dotted lines, (d) corresponding simulated powder X-ray diffractogram of rutile at Cu X-rays wavelength, (e) corresponding simulated powder X-ray diffractogram of 50:50 by volume mixture of rutile and anatase at Cu X-rays wavelength. The crystalline phase responsible for each peak in the diffractogram is marked as "A" (anatase) or "R" (rutile). (Crystal structures drawn by Ian Swainson using the CrystalMaker software, patterns calculated using PowderCell.)

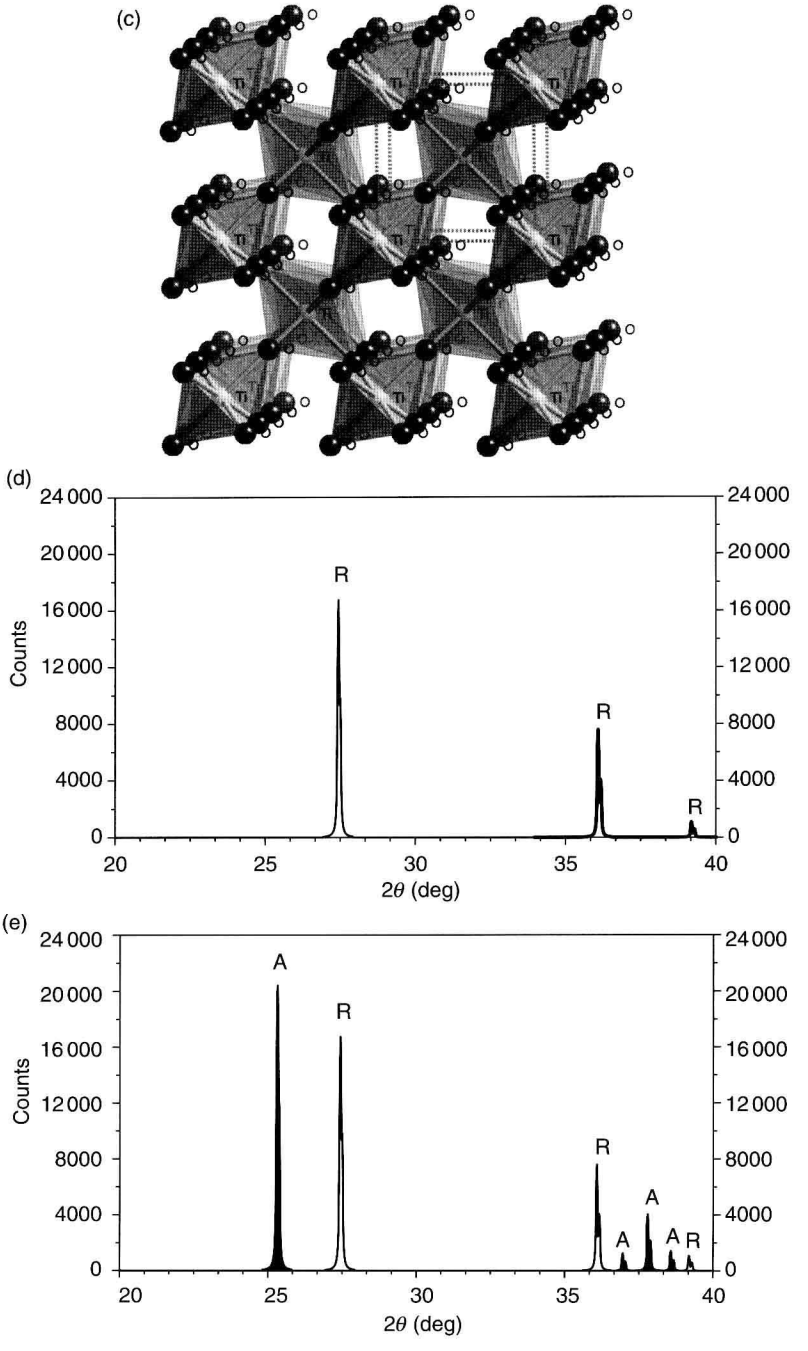

Figure 1.3 Continued.

dioxide, rutile and anatase, despite them being of identical elemental composition (TiO_2). With modern, optimized diffraction hardware and analysis software, phase identification of a routine sample, starting from grinding it to a powder to complete analysis, can be performed in the order of 5–15 min, where the actual data collection may take in the order of a minute or two depending on the diffractometer configuration and detector. Figure 1.4a shows an example of a modern commercial powder X-ray diffractometer goniometer in Bragg–Bretano reflection geometry mode, with X-ray tube housing on the left, single sample

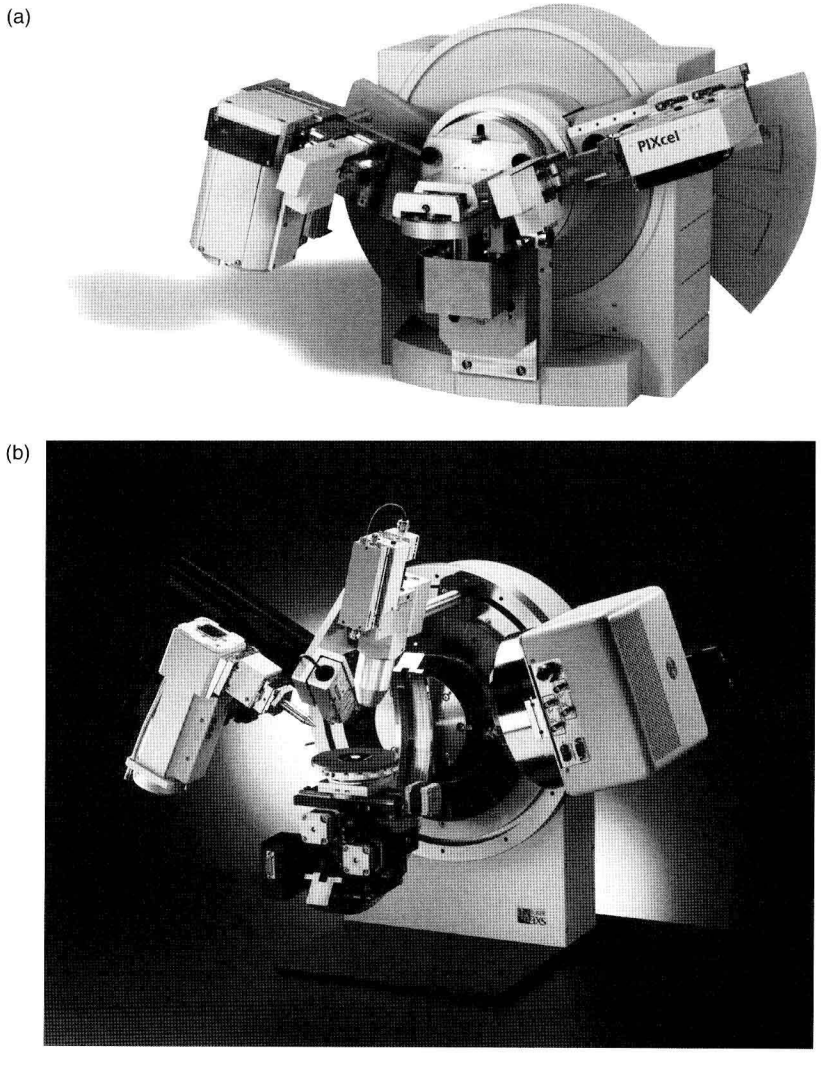

Figure 1.4 (a) Goniometer of modern commercial powder X-ray diffractometer in Bragg–Bretano reflection geometry mode and multi-element detector. (Photograph courtesy of PANalytical.) (b) A modern commercial microdiffractometer with 2D detector, including computer-controlled translators for 2D phase mapping. (Photograph courtesy of Bruker AXS.)

stage in the rotation center of the goniometer and multielement detector on the right. An installed system would include an X-ray generator, and a fully interlocked radiation enclosure consistent with radiation protection regulations. Figure 1.4b shows a commercial microdiffractometer with 2D detector, which can non-destructively obtain powder diffraction patterns of small targeted areas and 2D phase maps from samples such as mineralogical thin sections, metals, artworks, forensic materials, corrosion layers, deposits, and so on (see Sections 1.3.2, 1.6.2, 1.7.3, 1.7.10 and 1.7.16).

The above describes a routine and common usage of PXRD for phase identification and is elaborated in Chapter 6. Specialized use of powder diffraction can quantify phase amounts (Chapters 6 and 8); solve crystal structures (Chapter 7); and refine crystal structures (Chapter 8); determine micro-structural characteristics such as crystallite size, shape and strain (Chapter 9); identify the spatial distribution of phases down to the micron level using mapping microdiffraction (Chapter 3); and investigate phase stability and reactions under a range of different conditions such as time, temperature, pressure and atmosphere (Chapter 9). Laboratory based X-ray diffractometers are most commonly used for diffraction analysis, but electrons, and non-laboratory sources such as synchrotron X-rays and neutrons can also be applied in cases where they offer distinct advantages (Chapter 5).

Modern powder diffraction is computer intensive and requires a data analysis capability. A variety of general and specialist diffraction analysis software is available from commercial vendors, or freely available via the Internet. As is re-emphasized below, much of this software incorporates the expertise of their authors to an extent where a new user of diffraction can apply it to many nontrivial problems at the push of a button. A list of X-ray powder diffraction software is described in Appendix A.1.

1.2 Range of fields using powder diffraction

The usefulness of powder diffraction ranges throughout all areas where materials occur in the crystalline solid state. Uses for powder diffraction are found within the following fields and beyond:

1 Natural Sciences
2 Materials Science
3 Pharmaceuticals
4 Geology and Petrochemicals
5 Engineering
6 Metallurgy
7 Forensics
8 Conservation and Archaeology

Applications are elaborated in Section 1.7.

1.3 Advantages of powder diffraction

Potential users of powder diffraction are not immune from being busy in their working hours. Therefore, any technique wishing their attention must quickly justify itself and its