Synthesis, Properties and Mineralogy of Important Inorganic Materials

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For Kasper and Lars,
and in memory of the late Professor
Hans Toftlund

Contents

Foreword

This book is both timely and essential as, at present, there is a decline in the interest in inorganic chemistry as more and more bio related courses are introduced into University curricula. It is important to rectify this situation as the synthesis of inorganic materials with important physical and chemical properties will underpin many of the innovative industries of the future, and these industries will depend on the skills taught in this book. This applies especially to start-up companies where these specialist skills can be used to create novel products without an enormous capital investment. Given the present content of many courses, there is a dearth of trained scientists in this area. A significant number of the novel materials for the future will be synthesised by the techniques described in this book that meets a pressing need as chemists, physicists and materials scientists lacking in these essential skills from their undergraduate studies, can quickly learn the necessary techniques in order to make high-purity materials with the required properties.

Terence Warner has created a scholarly work that describes the synthesis of a selection of modern and ancient inorganic materials within the context of their mineralogy, properties and applications, which support many of our industries. It is informative to read how many of our advanced materials, or their closely related analogues, occur in nature. The text covers a wide range of materials from minerals that have been known to mankind for several generations, up to the latest synthetic electroceramic phases.

For graduate students and others who require a source of these materials for the study of their physical properties, it is always better and, perhaps, more satisfying, to prepare their own materials rather than rely on a supply from third parties. Furthermore, it is always preferable to synthesise the materials in-house so that a much greater understanding of the materials is obtained and the purity is assured. Although this book is primarily directed to final-year undergraduates and postgraduates, it also gives an excellent resume of the skills that had previously been taught in Universities for those working in industry. There is a continuing link between university research and industrial aspirations throughout this book.

Attention is also paid to the health and safety aspects of the preparations. Again, with a much greater emphasis on health and safety in Universities, some Departments are reluctant to undertake experiments involving high-temperature conditions and molten phases. This book very clearly demonstrates that it is possible to make these materials, without undue risk, using chemicals and equipment that are relatively cheap. For example, small pottery kilns are much cheaper than furnaces, yet deliver the same performance.

Overall, materials chemistry is an exciting area and this book ensures that the skills necessary to synthesise the relevant materials have been documented in a single volume. This book includes the science associated with the materials and their history of development and their applications, interspersed with fascinating facts, which makes a joy to read and, at the same time, for the reader to be stimulated.

Professor Derek J. Fray, *FREng FRS*
Cambridge

Preface

The synthesis of high-quality material is an essential step in the process of obtaining meaningful information about the material's properties, and therefore, is an important link between physics and chemistry. Semiconductors; superconductors; solid-electrolytes; glasses; pigments; dielectric, ferroelectric, thermoelectric, luminescent, photochromic and magnetic materials; are technologically important classes of material, that are represented by numerous inorganic phases. Yet how many of us are aware of their precise chemical compositions, and have sufficient knowledge to actually make them?

This book attempts to address this problem by offering the reader clear and detailed descriptions on how to prepare a selection of fifteen inorganic materials that exhibit important optical, magnetic, electrical and thermal properties; on a laboratory scale. The materials and chemical syntheses have been chosen so as to illustrate the large variety of physicochemical properties encountered in inorganic materials, and to provide practical experience covering a wide range of preparative methods, with an emphasis on high-temperature techniques. The majority of the materials described in the book relate to the macroscopic state and are prepared as polycrystalline materials. Several of these are fashioned into ceramic monoliths, whilst a few are retained in powder form or as single crystals.

The reader is given guidance, for example, to the quantities of material to prepare; sizes and types of crucibles and ampoules; use of furnaces; reaction times; heating and cooling rates; materials handling, such as, milling, mixing and separation procedures; multistage preparations; and the fabrication of ceramic monoliths. This book therefore aims at removing the rather abstract mysteries of chemical formulation and preparative methodology, whilst at the same time, focusing on the technologically important business of synthesising electroceramic materials.

The book is based on fifteen case studies, which illustrate how the properties of materials and the methods adopted for their syntheses, are dependent upon the chemical nature of the elements from which they are composed. Five of these materials contain the element copper situated in different chemical environments, which creates a convenient forum to discuss various topics, including: chemical affinity; electronegativity; acid–base chemistry; oxidation states; coordination chemistry; chemical bonding; electronic structure; crystal structure; and defect chemistry. These discussions extend throughout the book to incorporate the other ten materials.

Many useful ideas concerning this subject can be gained from a knowledge of mineralogy; which involves the study of naturally occurring inorganic crystalline phases. Therefore, references to mineralogy are made throughout the book. However, it is not essential for the reader to have a prior knowledge of mineralogy in order to understand the text since there are plenty of footnotes offering explicit information regarding mineralogical terminology. Likewise, certain historical details are included, so as to bring some of the curious tales surrounding the discovery of these materials, and the development of their syntheses, to the reader's attention.

The book has been written primarily for senior undergraduate and postgraduate students, and is intended to serve as a textbook for laboratory courses in chemistry, ceramics, materials science, and solid state physics degree programmes. It is written in a style that should encourage students to make the transition from *reading* to *researching* for their degree, and thereby help bridge the gap between conventional textbooks on the subject, and the research literature as published in scientific journals.

Many researchers working today in the field of materials science and technology have a background that may not have equipped them with sufficient chemical knowledge in order for them to prepare their own materials. This is often the case for newly graduated physicists, geologists and engineers who are engaged with postgraduate or postdoctoral research, where they are obliged to prepare inorganic materials as part of their research activities. This book should be of benefit to them. For instance, after attempting the syntheses described in this book, the reader should have acquired sufficient skills and knowledge so as to be able to prepare many similar and, unusual, inorganic materials.

The book is of appeal to university lecturers and school teachers who are interested in extending their repertoire of teaching material into the realms of high-temperature synthesis. It is also of interest to professional chemists, physicists, materials scientists and technologists, ceramicists, mineralogists, geologists, geochemists, archaeologists, metallurgists, engineers, and nonspecialists, who are interested in learning more about how inorganic materials and artificial minerals are made.

Finally, the author assumes that the reader is familiar with the basic principles and concepts of materials chemistry (or at least has access to such knowledge), such as: thermodynamic equilibrium; interpreting phase diagrams; chemical bonding; crystal structure; powder X-ray diffractometry;

optical and electron microscopy; crystal defects and Kröger–Vink notation; and the properties of materials. These subjects are covered extensively in undergraduate and postgraduate textbooks on physical chemistry; inorganic chemistry; solid-state chemistry; solid-state physics; materials chemistry; and mineralogy; and so they will not be repeated here. In this respect, the various footnotes refer the reader to a selection of relevant texts.

Acknowledgements

I wish to begin by thanking Dr Adam N. Bowett and Professor Keith Murray for encouraging me to put pen to paper and write this book. The nature of the subject brought me into dialogue and correspondence with numerous persons from a diverse range of professional backgrounds. I very much appreciate their willingness to share their knowledge and to provide literary and illustrative material, translations and experimental data. Consequently, I am grateful to Professor Andrew Bond, Professor John R. Cooper, Professor Judith L. Driscoll, Dr Mark Dörr, Professor Peter P. Edwards, Professor Dr Mohammed Es-Souni, Kristine Gable, Associate Professor Per Lyngs Hansen, Dr Yvonne Harpur, Associate Professor Ole Johnsen, Dr Dedo von Kerssenbrock-Krosigk, Associate Professor Venkatesan Manivannan, Associate Professor Per Morgen, Dr Boujemaa Moubaraki, Assistant Professor Ulla Gro Nielsen, Dr Ngo Van Nong, Associate Professor Ole V. Petersen, Associate Professor Victor V. Petrunin, Associate Professor Birte Poulsen, Dr Nini Pryds, Associate Professor Kaare L. Rasmussen, Professor Thilo Rehren, Dr Chris J. Stanley, Associate Professor Paul C. Stein, Mrs Sylvia Swindells, Professor Emeritus Michael S. Tite, Mary E. Vickers, Associate Professor Stefan Vogel, Nicola Webb, Professor Mark T. Weller, Associate Professor Emeritus Ole Wernberg, Professor Emeritus Jaime Wisniak, Dr Chris J. Wright and Dr Jianxiao Xu.

I am also grateful to my students who performed the syntheses, and in certain instances, some of the research described in the book. I also convey my thanks and appreciation for the technical assistance given by Mrs Susanne J. Hansen, Mr Poul Bjerner Hansen, Mr Torben H. Jensen and Mr Tommy Nørnberg.

I thank the referees (who remain anonymous to me) for their comments and suggestions regarding my original proposal. I also express my deep gratitude to Professor Derek J. Fray, dr. techn. Finn Willy Poulsen, Dr Nevill M. Rice and Professor Eivind M. Skou for reading the typescript and offering their constructive criticisms and comments. Their efforts have helped enormously to improve the book. It is, however, only fair to add that I remain entirely responsible for all errors and inconsistencies in the published text.

I also wish to thank Associate Professor Ole Johnsen, for kindly allowing the reproduction of four of his photographs of mineralogical specimens in this book; three of these were published originally in *Mineralernes Verden* (GadsForlag, 2000). I am also sincerely grateful to Professor Derek J. Fray for writing the Foreword.

I thank my wife, Tine, for her unremitting support that ensured the completion of this work. Sadly, whilst I was writing this book, my colleague and friend Professor Hans Toftlund passed away. I wish to express my appreciation for the knowledge and inspiration that Hans so generously gave me and that created the foundation for this book. His company is greatly missed.

Finally, I wish to express my thanks to my publishers for their enthusiastic and helpful co-operation throughout the production of this book, and particularly to Alexandra Carrick, Richard Davies, Jon Peacock and Emma Strickland for their editorial advice and guidance.

1

Introduction

There is an island off the west coast of Scotland whose name is given to a mineral that was first discovered there by Bowen *et al.* in 1924 [1]. The mineral occurs within an argillaceous rock[1] that has undergone thermal metamorphism[2] as a consequence of becoming entrapped within a hot magma during the Tertiary period. The mineral is quite remarkable in that the synthetic equivalent is produced within terra-cotta[3] (baked clay) and thereby must surely represent one of the earliest crystalline inorganic ternary phases prepared artificially by mankind. Furthermore, terra-cotta artefacts have been fabricated since antiquity; thus marking the advent of ceramics, both as a material and a subject.

The mineral in question is *mullite*, as from the Isle of Mull, Scotland. Mullite has a chemical composition corresponding to the solid-solution series, $Al_{4+2x}Si_{2-2x}O_{10-x}$ $(0.17 \leq x \leq 0.59)$, and occurs as tiny colourless acicular crystals that are normally invisible to the naked eye (see Figure 1.1). It has a crystal structure closely related to sillimanite, Al_2SiO_5 (the mineral that it was originally mistaken for); but it is commonly reported as simply, $3Al_2O_3{\cdot}2SiO_2$ [2]. Mullite is formed in nature under the unusual geological conditions of high temperature and low pressure (corresponding to the sanidinite facies: $T = 800 - 1000\,^{\circ}C$ and $p \leq 2\,kbar$) and is found in certain metamorphic glassy rocks, such as buchite [3].

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1 *Argillaceous rocks* are a group of sedimentary rocks (e.g., clays, mudstones, shales and marls) that have a high content of clay minerals.
2 *Thermal metamorphism* is the process by which rocks within the earth's crust are altered under the influence of heat alone; cf. contact metamorphism.
3 *Terra-cotta* is a crude earthenware that is usually brownish-red due to the presence of hematite, Fe_2O_3 cf. the more refined potteries e.g., faience, stoneware and porcelain.

Synthesis, Properties and Mineralogy of Important Inorganic Materials By Terence E. Warner

Figure 1.1 Scanning electron micrograph of mullite needles formed hydrothermally in small druses of volcanic rocks of the Eifel mountain, Germany (Reproduced with permission from Mullite by H. Schneider, Fig. 1.3, xvii, Edts. H. Schneider and S. Komarneni, Copyright (2005) Wiley-VCH)

When ball clay (a natural earthy mass of kaolinite, $Al_2Si_2O_5(OH)_4$ and other clay minerals) is heated artificially, it first undergoes dehydration, followed by an exothermic reaction at $\sim$950 °C, where upon the dehydrated material transforms into an impure composite of mullite, β-quartz and γ-alumina; commonly known as terra-cotta. This is a complex metastable system in which the fraction of mullite increases with annealing time and temperature, at the expense of β-quartz and γ-alumina. Hence, ordinary pottery is a more intricate material than what first meets the eye. Given the primitive conditions under which terra-cotta was prepared by prehistoric man, it is not too surprising that this material comprises the three most abundant elements in the earth's crust, namely; oxygen, silicon and aluminium. This also reflects the ubiquitous nature of the clay minerals, which can be collected quite readily with bare hands, from surface deposits.[4]

Terra-cotta artefacts have been manufactured in Mesopotamia since at least 6000 BC [6].[5] This predates the smelting of copper and the synthesis of

[4] The vast majority of clay minerals are essentially hydrous aluminium silicates. The reader is referred to Schneider and Komarneni [4] for further details regarding the subject of mullite; and to Holdridge and Vaughan [5] for details concerning the thermal treatment of kaolin.

[5] *TheTerracotta Army* of Qin Shi Huang the First Emperor of China, discovered near Xi'an Shaanxi province, China, is estimated to comprise over 8000 terra-cotta figures (mostly depicting soldiers as life size), and is an impressive example of the use of terra-cotta dating from *ca.* 210 BC.

Figure 1.2 Nest of triangular crucibles recovered in Hesse (Photograph used with kind permission from S. Häpe, courtesy of H.-G. Stephan Copyright (2006) H.-G. Stephan)

the copper–arsenic and copper–tin alloys (*ca.* 3500 BC). The usefulness of terra-cotta vessels (pots, beakers, crucibles, etc.), particularly those with a high content of mullite, cannot be over emphasised. Historically, their fabrication was a prerequisite for the smelting of metals, and thus the development of metallurgy per se. The famous Hessian mullite crucibles fabricated since the 12^{th} century at Epterode and Almerode (now; Großalmerode), in the region of Hesse, Germany, were renowned for their refractoriness, and represent the earliest industrial exploitation of mullite in Europe (see Figure 1.2) [7, 8].

Throughout history, terra-cotta vessels of various qualities, have been used for the preparation of many other useful substances, such as, zythum,[6] pigments and glass, as well as for the practices that led to the development of chemistry. Indeed, the very word *chemistry* is considered to have derived from the Arabic *al-kimia*, through the transliteration of the Greek *χυμεία* (*khymeia*; in English *pouring*) in connection with the *infusion* of plants for pharmaceutical use [9], and the *casting* of metals.[7] The point being stressed here is that in order to prepare a chemical substance, particularly when the process involves liquids or operating at high-temperature, the practitioner

[6] *Zythum* was a drink made in ancient times from fermented malt, especially in Egypt.
[7] The popular association of *al-kimia* (in English *alchemy*) with the native name of Egypt, *Khem* ('land of black earth' cf. Plutarch *ca.* 100 AD), by allusion to the black soil of the Nile delta in contrast to the desert sand – hence, 'the art of the black earth' in reference to the pursuits of the Alexandrian alchemists in Hellenistic Egypt– is considered by Mahn [9] to be a subsequent development of the subject, and that the origin of the word is most probably Greek [9].

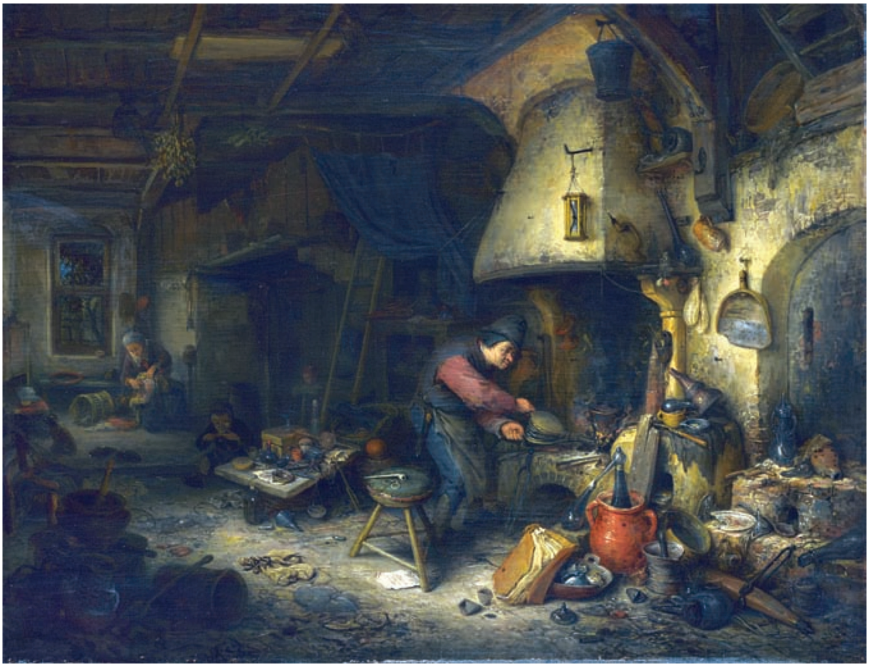

Figure 1.3 *An Alchemist*, 1661, Adriaen van Ostade (1610–1685). Note the triangular crucibles in the foreground, and the importance of heat for inducing a change in chemical substances (Reproduced with permission. Copyright National Gallery, London)

must first of all acquire a suitable container in which to conduct the synthesis; an aspect that is of course, still very relevant today.

Chemistry as a scientific discipline grew out of the magical practice of alchemy in Europe during the Middle Ages. One of the main aspects of alchemy involved serious practical attempts at making gold through the transmutation of the less noble metals;[8] and was accompanied by general random experiments with various metals, minerals, salts, acids, gums and chemical extractions, often at elevated temperature. Given the high value of gold, and the heinous punishments meted out by the Church for deviant behaviour, alchemists devised their own mysterious symbolisms for describing their preparative procedures, such that their work was generally shrouded in secrecy. The painting of '*An Alchemist*' by Adriaen van Ostade, casts a satirical portrayal of these futile activities during the 17th century (see Figure 1.3). Coincidentally, Ostade painted '*An Alchemist*' in the same

[8] In particular; mercury, copper, tin and lead.

year, 1661, that Robert Boyle wrote '*The Sceptical Chymist*'; which marks a turning point in the transition between alchemy and chemistry.[9] Although these attempts at making gold were of course all in vain, it is through these practical activities that alchemy transformed into scientific pursuits, such as the chemical analysis of minerals and the discovery of the chemical elements and their compounds. These in turn, led to commercial enterprises like the production of European porcelain, and eventually, the modern ceramic and giant electronics industries.

The roots of chemistry, therefore, lie deeply in the intermingled business of synthesis and analysis; in which synthesis can be defined as the art of bringing about purposeful changes in chemical substances. The principle role of the chemist is to investigate the various substances of which matter is composed, and thereby acquire knowledge of their chemical nature, in terms of composition, structure, affinity and reactivity; and develop methods for their synthesis.

Chemistry has often been closely associated with mineralogy. During the 18^{th} and 19^{th} centuries it became very much a gentleman's pursuit to perform chemical analyses on the numerous mineral species that were being discovered during this period of scientific enlightenment. Furthermore, a definitive way to prove the existence of a new mineral species was to synthesise its artificial equivalent. It is also important to remember that all chemical substances are derived ultimately from terrestrial and extraterrestrial resources, of which minerals are by far the major part. Today, although the recycling of spent materials constitutes an important economic resource, minerals still remain the primary source of industrial raw materials; and that includes the feedstock for inorganic chemical reagents.

Minerals constitute a large body of crystalline inorganic compounds, and the mineralogical literature contains valuable information concerning their chemical composition, crystal structure, physical properties and paragenesis.[10] Certain minerals, for example; scheelite, $CaWO_4$; magnetite, Fe_3O_4; and quartz, α-SiO_2; have inspired technological applications directly on account of their luminescent, magnetic and piezoelectric properties, respectively. The rare mineral lazurite, $(Na,Ca)_8[Al_6Si_6O_{24}](Cl,SO_4,S)_{2-\delta}$ has been used as a blue pigment since antiquity and was literally worth its weight in gold. Attempts at synthesising its artificial equivalent presented some considerable challenges in both analytical and preparative chemistry. But eventually, in 1828, with the enticement of a prize worth 6000 francs from the *Société d'encouragement pour l'industrie nationale*, Jean Baptiste Guimet

[9] It is interesting to note, that Isaac Newton (1642–1727) spent over 20 years practising alchemy in a garden shed at Trinity College, Cambridge [10].

[10] *Paragenesis* refers to the association of different minerals within the same deposit; and so reflects their origin (i.e., the conditions for their primary crystallisation and subsequent history) either collectively, or in reference to a specific mineral. The word *Paragenesis* is derived from ancient Greek; *Para-* meaning, along side; *–genesis* meaning, creation, origin.

succeeded in making artificial lazurite from kaolin;[11] and his efforts led to the commercial production of the pigment, *ultramarine* [11].

New mineral species continue to be discovered, and many of those that are known already have not yet been prepared artificially, for example, the gemstones; azurite, $Cu_3(CO_3)_2(OH)_2$; and dioptase, $Cu_6Si_6O_{18}\cdot 6H_2O$. This is just one of the reasons why the subject is so interesting. Certain workers have even coined the expression, *geomimetics*, to describe the imitation of geological materials, in an attempt to promote the subject from this perspective. In general terms, materials chemistry can be considered as a broad interdisciplinary field that embraces many of the chemical aspects of mineralogy, ceramics and metallurgy, and overlaps with archaeology and solid-state physics. The monograph by Ebelmen, Salvétat and Chevreul, published in 1861 and entitled, '*Chimie, Céramique, Géologie, Métallurgie*', bears testament to this [13].

Today, there are many books published that contain descriptions regarding preparative methods in solid state chemistry; but only a few are dedicated to the subject.[12] Collectively, they represent a very significant source of knowledge and inspiration, but with the notable exception of *Wold and Dwight*, they all focus on methodology and experimental techniques. Examples of real materials, when given, are usually written in the spirit of exemplifying the technique, rather than offering the reader clear and detailed preparative instructions of how to make the material. On the other hand, the preparative methods reported in scientific journals tend to be rather brief, especially those published in recent years. Consequently, many of the descriptions reported in the literature concerning the preparation of inorganic materials can be difficult to follow. So, for students, and postdoctoral workers new to the field, this can present a genuine problem.

This book was written with that problem in mind. Therefore, it can be considered primarily, as a guide to the synthesis of inorganic materials, and offers the reader comprehensive and detailed step-by-step instructions, in order to prepare a selection of materials on a laboratory scale. Since the properties of these materials are of inherent scientific and technological importance, it is necessary to discuss these in reasonable detail. The book describes a series of case examples that involve a wide range of preparative techniques. These have been selected to ensure that they are practically feasible, given normal laboratory facilities, and yet retain a certain challenge to the reader. The subject matter dealing with methodology and experimental

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[11] Ultramarine can be prepared industrially by heating a blended mixture of kaolin (essentially, kaolinite, $Al_2Si_2O_5(OH)_4$), sodium carbonate, silica, sulfur and coal tar pitch to 750–800 °C for 50–100 h, followed by slow cooling over several days under an oxidising atmosphere [12].

[12] For example; *Inorganic Materials Synthesis and Fabrication' by* Lalena *et al.* [14]; '*Synthesis of Inorganic Materials*,' by Schubert and Hüsing [15]; '*Solid State Chemistry: Synthesis, Structure, and Properties of Selected Oxides and Sulfides*' by Wold and Dwight [16]; and, '*Chemical Synthesis of Advanced Ceramic Materials*' by Segal [17].

techniques are described in many excellent texts and therefore is not covered in great detail here.

The philosophy of the book is to show, through the descriptions of real chemical systems, how the properties of a material can be influenced by modifications to the preparative procedure by which the material is made; and vice versa. For instance, the nature of the chemical reagents, the impurities and the thermal history, can have a profound effect on the product material, especially with regards to chemical composition, homogeneity, crystal structure, morphology, microstructure, and thus, its physical properties. Conversely, the requirement for a specific property within a given material will normally dictate certain details in the course of its preparation. Furthermore, the production of phase-pure material is normally a prerequisite for any meaningful characterisation and exploitation of the material. But in reality, this is often a difficult task, and so, before this goal can be achieved, many skills need to be developed and knowledge of the relevant chemical system acquired.

This book is a cross between a textbook and a monograph. The chapters are named according to chemical composition and preparative method. It was considered rather pointless, however, to place too much emphasis on categorising the materials according to a principle property, since in several cases they exhibit more than one. Although the chapters are essentially self-contained, it is assumed that they will be read in sequential order, for the sake of continuity of the story. In general, the International System of units, is used in this book, but there are occasions when matters of practicality or, common sense, dictate the use of the more appropriate units, such as; degrees Celcius, °C; bar; hour, h; minute, min; ångström, Å; litre, l; Bohr magneton, μ_B; oersted, Oe; and the electromagnetic unit, emu.

The illustrations of the crystal structures in this book were produced with ATOMS, by Shape Software,[13] using data from the Inorganic Crystal Structure Database (ICSD)[14] with reference to the original publications from which these data were compiled. In most cases the atomic and ionic radii are drawn smaller than in reality; thus enabling the reader to look into the interior of, or through, the unit cell. The E_H-pH diagrams were produced using Outokumpu HSC Chemistry® Software.[15] Certain phase equilibria diagrams from The American Ceramic Society[16] have been reproduced in this book and used with permission from the copyright holders of the original publications.

[13] Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663 USA.
[14] Inorganic Crystal Structure Database, Fachinformationszentrum, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Karlsruhe, Germany.
[15] Outokumpu HSC Chemistry® Software, Outokumpu Research Oy, Information Service, PO Box 60, FIN-28101 Pori, Finland.
[16] ACerS-NIST Phase Equilibria Diagrams, The American Ceramic Society, P.O. Box 6136, Westerville, OH 43086-6136, USA.

In order to perform the various syntheses, the reader may wish to use this book simply as a laboratory manual. Alternatively, after reading the book in more depth, the reader should be in a better position to embark on the business of making the inorganic materials that are required for his or her own research, or private interests. Finally, a set of problems is included at the end of each chapter for the reader's perusal. Suggested answers to these, together with formulations for the respective syntheses, can be made available to bona fide course instructors upon request, via; www.wiley.co.uk.

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2

Practical Equipment

This chapter offers information and practical advice about the equipment needed to perform the syntheses of the materials as described in the book. It does not discuss the principles of the methods employed, at least not in detail, since these are covered elsewhere in many excellent texts; nor does it describe the methods concerning the characterisation of materials, since these are referred to at the relevant places within the main body of the text. This chapter does include, however, certain practical information regarding powder X-ray diffractometry, because this is the principle technique used for the routine phase analysis of crystalline inorganic materials. In addition to the information given here, the reader is strongly advised to follow the manufacture's instructions when using the equipment referred to in this book.

2.1 CONTAINERS

One of the points raised in Chapter 1 is the importance of acquiring a suitable container in which to conduct the synthesis. Fundamentally, the reaction vessel must survive contact, not only with the chemical reagents and precursor compounds, but also with the product material, and any chemical species and intermediate phases produced during the course of the reaction. These requirements generally become more prohibitive as the temperature and pressure of the system is increased. Furthermore, the retrieval of product material that adheres to the walls of the container often presents an additional problem that needs to be considered when devising a preparative method.

Beakers and flasks made of Pyrex™ glass are quite adequate for handling the majority of the aqueous solutions and precipitated material described in

Synthesis, Properties and Mineralogy of Important Inorganic Materials By Terence E. Warner

this book. Pyrex™ glass has excellent corrosion and thermal-shock properties that make it ideally suited for general use in preparative chemistry; at least at temperatures below 500 °C. For operations above 500 °C, a container made from a more resilient material is needed.

Porcelain crucibles find popular use in conventional chemical laboratories, and serve well for many of the preparations performed in analytical chemistry that require moderate heating, for example, with a Bunsen burner. Porcelain is a composite material comprising an entangled mass of acicular crystals of mullite, $Al_6Si_2O_{13}$ dispersed within a silicate glass matrix; which results in a tough material with a high compressive strength and a good resistance to thermal shock. Porcelain crucibles are available; glazed[1] and unglazed. The reader should be aware of substances that can react with the glaze; and indeed with the glass phase within the porcelain itself. For instance, alkali metal oxides can diffuse into the glaze upon heating and thereby degrade the crucible. But in all cases, porcelain crucibles are not recommended for high-temperature or refractory use; especially since more suitable alternatives are commercially available.

From a conceptual point of view, eliminating the presence of the glass phase from a typical porcelain body, leads towards, a ceramic material comprising solely of mullite. Mullite is an important refractory material with a melting point of 1810 °C. It has an outstanding resistance to thermal shock, and in this respect is superior to recrystallised alumina, even though alumina has a higher melting point of 2040 °C. For these reasons, mullite crucibles are used extensively in the melting of iron alloys, the base metals and their alloys. Nevertheless, one should be aware that mullite contains a significant amount of chemically combined 'SiO_2' that can be reactive towards certain metal oxides at high temperature. The manufacturing of mullite crucibles is generally more demanding than that for porcelain, and so they command a higher price.

This leads to recrystallised alumina, Al_2O_3 as the preferred choice of crucible material for many of the preparative descriptions in this book;[2] see Figure 2.1. Recrystallised alumina crucibles have limitations as well, of course. Although they are densely sintered, they are nevertheless prone to react with certain chemical substances within systems in which free alumina, Al_2O_3 finds itself thermodynamically unstable. For example, Al_2O_3 is unstable in the presence of the copper oxides, CuO, and Cu_2O, with respect to the formation of the ternary phases, $CuAl_2O_4$, and $CuAlO_2$; which can manifest as surface coatings on the inner walls of the alumina crucible. This is

[1] A glaze is a thin layer of glass used as a protective coating; commonly used to render pottery impermeable to fluids, and to avoid entrapment of powdered material, dust, etc.

[2] The alumina crucibles used in the practical work as described in this book were supplied by Almath Crucibles Ltd., Epsom Building, The Running Horse, Burrough Green, Nr Newmarket, Suffolk, CB8 9NE, United Kingdom.