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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

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[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 12th 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

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[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. Adriaen van Ostade, An Alchemist © The 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

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[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 18th and 19th 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

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[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, $Cu_6Si_6O_{18}\cdot6H_2O$. 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.

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[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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