Synthesis of Inorganic Materials
Synthesis of Inorganic Materials

Ulrich Schubert
Nicola Hüsing

Fourth Edition
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Preface

When the first edition of *Synthesis of Inorganic Materials* was published in 2000, we had hoped that the book would make the role of chemistry in materials science more visible, especially to students, and would provide an overview of chemical methods for the synthesis of inorganic materials. In the meantime, the textbook is an established source in many chemistry and materials science curricula. The success of the first three editions and the very positive feedback encouraged us to revise and update the book. We hope that the fourth edition will continue to have impact on the teaching of materials chemistry and materials science in general.

In most materials science and solid-state chemistry textbooks – even highly recommended ones – there is a regrettable lack of chemical information. Materials science is often reduced to physical and technological aspects, and processes for the preparation and modification of materials – the most important contribution of chemistry – are mostly treated just in passing or perhaps not at all. With this textbook we are attempting to fill this gap. The book is not intended as a substitute for existing physically or technologically oriented textbooks on materials science, but rather to complement chemical aspects. The nucleus of this book was lecture courses given by the authors at the Vienna University of Technology and the University of Salzburg.

This textbook is intended for use not only by chemistry students (for whom, we have tried to keep the number of physical formulae at a minimum) but also by physics and materials science students (for whom, we have tried to keep the required chemical prerequisites at a minimum). The glossary may help to bridge the gap between chemical/physical/materials science fundamentals. At the end of each chapter, a selection of some books and review articles is provided, which may help the reader to study those processes under discussion in greater detail. In order to stay as close as possible to the real world of materials science, we have tried to introduce relevant technically applied materials in many sub-chapters.

The fourth edition was completely revised and updated, putting even more emphasis on synthesis and modification techniques than in the previous editions. Chapter 6 is dedicated to materials based on self-assembly processes, and the chapters on templating strategies and nanomaterials were largely rewritten. Most of the other chapters were restructured as well. We have also covered additional preparation methods that were not or only incidentally covered in the previous editions, such as the citrate–gel method, CVD of elemental silicon and graphene, shape control of crystals, electrodeposition of ceramics, preparation of porous
metals by electrochemical oxidation, syntheses of hollow particles, breath figures templating, freeze casting, evaporation-induced self-assembly, or pseudomorphic transformations. Many new figures were included, as well as new application examples, such as the materials basis of metallic glasses, LEDs, lithium-ion batteries, or drug delivery by porous nanoparticles.

In an up-to-date textbook, SI units should be used exclusively. However, different scientific communities still have their own habits concerning physical units (for example, ceramists prefer Pascal, while CVD people prefer bar or atmosphere as the pressure unit). We therefore decided to leave some transformations of physical units to the reader – with the help of a table at the inner cover of the book.

Traditional classifications of materials (natural materials, metals, non-metallic inorganic materials, organic polymers, composite materials, and so on) are based on composition or some fundamental properties and somehow also reflect the different structural and bonding features. In this book, we want to emphasize the chemical aspects, and therefore the book is organized according to methods for the preparation, transformation, and modification of inorganic materials, highlighting the concomitant changes in composition, structure, and properties. We therefore did not treat all major inorganic materials comprehensively, but selected examples to discuss the ways in which (natural or artificial) chemical compounds are transformed into materials. For the same reason, materials properties and technological aspects are discussed only exemplarily.

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- **Degussa,** Hanau: the Aerosil process (Figures 3.26 and 3.27).
- **Department of Materials Science, University of Erlangen-Nürnberg** (Prof. Dr. Peter Greil): biomorphic SiC ceramics (Figure 2.12).
- **Fraunhofer-Institut für Silicatforschung,** Würzburg (Dieter Sporn and Dr. Klaus Rose): sol-gel materials (Figures 4.52, 4.68, and 4.69).
- **Hoechst AG,** Frankfurt: aerogels (Figure 4.73).
- **NASA/JPL-Caltech** (David C. Agle): aerogels for the Stardust mission (Figure 4.74).
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- **Wacker-Chemie,** Burghausen (Dr. Johann Weis): silicones (Figures 5.2 and 5.3).

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### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AACVD</td>
<td>aerosol-assisted chemical vapour deposition</td>
</tr>
<tr>
<td>ac</td>
<td>alternating current</td>
</tr>
<tr>
<td>Ac</td>
<td>acetyl</td>
</tr>
<tr>
<td>acac</td>
<td>acetylacetonate = 2,4-pentanedionate</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>AIBN</td>
<td>azobis(isobutynitrile)</td>
</tr>
<tr>
<td>ALD</td>
<td>atomic layer deposition</td>
</tr>
<tr>
<td>ALE</td>
<td>atomic layer epitaxy</td>
</tr>
<tr>
<td>AO</td>
<td>atomic orbital</td>
</tr>
<tr>
<td>aq</td>
<td>aqueous</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>au</td>
<td>arbitrary units</td>
</tr>
<tr>
<td>BBU</td>
<td>basic building unit</td>
</tr>
<tr>
<td>BMG</td>
<td>bulk metallic glass</td>
</tr>
<tr>
<td>b.p.</td>
<td>boiling point</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>C</td>
<td>critical point</td>
</tr>
<tr>
<td>cat</td>
<td>catalyst</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CBE</td>
<td>chemical beam epitaxy</td>
</tr>
<tr>
<td>CBU</td>
<td>composite building unit</td>
</tr>
<tr>
<td>CDJP</td>
<td>controlled double jet precipitation</td>
</tr>
<tr>
<td>cmc</td>
<td>critical micelle concentration</td>
</tr>
<tr>
<td>CMC</td>
<td>ceramic matrix composite</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl or heat capacity</td>
</tr>
<tr>
<td>CTAB</td>
<td>cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapour deposition</td>
</tr>
<tr>
<td>CVI</td>
<td>chemical vapour infiltration</td>
</tr>
<tr>
<td>D</td>
<td>dimensional or diffusion coefficient</td>
</tr>
<tr>
<td>dc</td>
<td>direct current</td>
</tr>
<tr>
<td>DLICVD</td>
<td>direct liquid injection CVD</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>diglyme</td>
<td>diethyleneglycol dimethylether</td>
</tr>
<tr>
<td>diphos</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>dpm</td>
<td>dipivaloylmethanate (=thd or tmhd)</td>
</tr>
<tr>
<td>dpnp</td>
<td>1,3-bis(diphenylphosphino)propane</td>
</tr>
<tr>
<td>EDTA</td>
<td>(ethylenedinitrilo)tetraacetic acid</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi energy (Fermi level)</td>
</tr>
<tr>
<td>EISA</td>
<td>evaporation-induced self-assembly</td>
</tr>
<tr>
<td>EPD</td>
<td>electrophoretic deposition</td>
</tr>
<tr>
<td>Eq.</td>
<td>equation</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centred cubic</td>
</tr>
<tr>
<td>G</td>
<td>free energy</td>
</tr>
<tr>
<td>g</td>
<td>gaseous</td>
</tr>
<tr>
<td>GMR</td>
<td>giant magnetoresistance</td>
</tr>
<tr>
<td>GO</td>
<td>graphene oxide</td>
</tr>
<tr>
<td>$H_c$</td>
<td>coercivity</td>
</tr>
<tr>
<td>HA</td>
<td>hydroxylapatite</td>
</tr>
<tr>
<td>Hex</td>
<td>hexyl</td>
</tr>
<tr>
<td>hdp</td>
<td>hexagonal dense packing</td>
</tr>
<tr>
<td>hfac</td>
<td>1,1,1,5,5,5-hexafluoracetylacetonate (1,1,1,5,5,5-hexafluoro-2,4-pentanedionate)</td>
</tr>
<tr>
<td>HIP</td>
<td>hot isostatic pressing</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTV</td>
<td>high-temperature vulcanizing</td>
</tr>
<tr>
<td>IEP</td>
<td>isoelectric point</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>L</td>
<td>ligand or Lewis base</td>
</tr>
<tr>
<td>l</td>
<td>liquid</td>
</tr>
<tr>
<td>LbL</td>
<td>layer-by-layer technique</td>
</tr>
<tr>
<td>LC</td>
<td>liquid crystal or liquid crystalline</td>
</tr>
<tr>
<td>LCVD</td>
<td>laser-assisted or laser-induced CVD</td>
</tr>
<tr>
<td>LDH</td>
<td>layered double hydroxide</td>
</tr>
<tr>
<td>LED</td>
<td>light-emitting diode</td>
</tr>
<tr>
<td>Ln</td>
<td>lanthanoid</td>
</tr>
<tr>
<td>LPCVD</td>
<td>low-pressure CVD</td>
</tr>
<tr>
<td>LPS</td>
<td>liquid-phase sintering</td>
</tr>
<tr>
<td>LR</td>
<td>liquid rubber</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>μCP</td>
<td>microcontact printing</td>
</tr>
<tr>
<td>M</td>
<td>molar or metal</td>
</tr>
<tr>
<td>MBE</td>
<td>molecular beam epitaxy</td>
</tr>
<tr>
<td>MCM</td>
<td>Mobil Composition of Matter</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>MPCVD</td>
<td>microwave plasma-assisted CVD</td>
</tr>
<tr>
<td>MLD</td>
<td>molecular layer deposition</td>
</tr>
<tr>
<td>MLE</td>
<td>molecular layer epitaxy</td>
</tr>
<tr>
<td>MMC</td>
<td>metal matrix composite</td>
</tr>
<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>MO...</td>
<td>metal–organic ...</td>
</tr>
<tr>
<td>MOF</td>
<td>metal–organic framework</td>
</tr>
<tr>
<td>MSI</td>
<td>metal–support interaction</td>
</tr>
<tr>
<td>MWNT</td>
<td>multiwalled nanotube</td>
</tr>
<tr>
<td>$n_D$</td>
<td>refractive index</td>
</tr>
<tr>
<td>NLO</td>
<td>non-linear optic</td>
</tr>
<tr>
<td>nm</td>
<td>nanometre</td>
</tr>
<tr>
<td>OAc</td>
<td>acetate</td>
</tr>
<tr>
<td>OM...</td>
<td>organometallic ...</td>
</tr>
<tr>
<td>$p$</td>
<td>para or pressure</td>
</tr>
<tr>
<td>$p_c$</td>
<td>critical pressure</td>
</tr>
<tr>
<td>PACVD</td>
<td>plasma-assisted CVD</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma-enhanced CVD</td>
</tr>
<tr>
<td>PEG</td>
<td>poly(ethylene glycol)</td>
</tr>
<tr>
<td>PEO</td>
<td>poly(ethylene oxide)</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>phen</td>
<td>phenanthroline</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methylmethacrylate)</td>
</tr>
<tr>
<td>PMC</td>
<td>polymer matrix composite</td>
</tr>
<tr>
<td>PMO</td>
<td>periodic mesoporous silica</td>
</tr>
<tr>
<td>POSS</td>
<td>polyhedral oligomeric silsesquioxane</td>
</tr>
<tr>
<td>PPO</td>
<td>poly(propylene oxide)</td>
</tr>
<tr>
<td>Pr</td>
<td>propyl</td>
</tr>
<tr>
<td>PZC</td>
<td>point of zero charge</td>
</tr>
<tr>
<td>PZT</td>
<td>lead zirconate titanate</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapour deposition</td>
</tr>
<tr>
<td>PVP</td>
<td>poly(vinylpyrrolidone)</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>R</td>
<td>organic group</td>
</tr>
<tr>
<td>r.f.</td>
<td>radio frequency</td>
</tr>
<tr>
<td>rGO</td>
<td>reduced graphene oxide</td>
</tr>
<tr>
<td>ROP</td>
<td>ring-opening polymerization</td>
</tr>
<tr>
<td>RPCVD</td>
<td>remote plasma chemical vapour deposition</td>
</tr>
<tr>
<td>RTV</td>
<td>room temperature vulcanizing</td>
</tr>
<tr>
<td>s</td>
<td>solid</td>
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<tr>
<td>S</td>
<td>solubility</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
</tr>
<tr>
<td>SBU</td>
<td>secondary building unit</td>
</tr>
<tr>
<td>SCF</td>
<td>supercritical fluid</td>
</tr>
<tr>
<td>sec</td>
<td>secondary</td>
</tr>
<tr>
<td>SCS</td>
<td>solution combustion synthesis</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SET</td>
<td>single-electron transfer</td>
</tr>
<tr>
<td>SHS</td>
<td>self-propagating high-temperature synthesis</td>
</tr>
<tr>
<td>SLS</td>
<td>solution–liquid–solid</td>
</tr>
<tr>
<td>SPD</td>
<td>severe plastic deformation</td>
</tr>
<tr>
<td>SSM</td>
<td>solid-state metathesis</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscope</td>
</tr>
<tr>
<td>SWNT</td>
<td>single-walled nanotube</td>
</tr>
<tr>
<td>$t_{\text{gel}}$</td>
<td>gel time</td>
</tr>
<tr>
<td>$T_{\text{ad}}$</td>
<td>adiabatic temperature</td>
</tr>
<tr>
<td>$T_{\text{b}}$</td>
<td>boiling temperature</td>
</tr>
<tr>
<td>$T_{c}$</td>
<td>critical temperature or Curie temperature</td>
</tr>
<tr>
<td>$T_{g}$</td>
<td>glass transition (glass transformation) temperature</td>
</tr>
<tr>
<td>$T_{\text{ig}}$</td>
<td>ignition temperature</td>
</tr>
<tr>
<td>$T_{m}$</td>
<td>melting temperature</td>
</tr>
<tr>
<td>TBA</td>
<td>tert-butylarsine</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TEOS</td>
<td>tetraethoxysilane (tetraethylorthosilicate)</td>
</tr>
<tr>
<td>TOPO</td>
<td>tri-$n$-octylphosphine oxide</td>
</tr>
<tr>
<td>tert</td>
<td>tertiary</td>
</tr>
<tr>
<td>thd</td>
<td>tetramethylheptanedionate (=tmhd or dpm)</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>tmhd</td>
<td>tetramethylheptanedionate (=thd or dpm)</td>
</tr>
<tr>
<td>TMOS</td>
<td>tetramethoxysilane (tetramethylorthosilicate)</td>
</tr>
<tr>
<td>Tr</td>
<td>triple point</td>
</tr>
<tr>
<td>TTT</td>
<td>time – temperature – transformation curve</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra-high vacuum</td>
</tr>
<tr>
<td>UHVCVD</td>
<td>ultra-high vacuum CVD</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>$V_{M}$</td>
<td>molar volume</td>
</tr>
<tr>
<td>Vi</td>
<td>vinyl</td>
</tr>
<tr>
<td>VLS</td>
<td>vapour–liquid–solid</td>
</tr>
<tr>
<td>VSS</td>
<td>vapour–solid–solid</td>
</tr>
<tr>
<td>VPE</td>
<td>vapour-phase epitaxy</td>
</tr>
<tr>
<td>wt</td>
<td>weight</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>YAG</td>
<td>yttrium aluminium garnet</td>
</tr>
<tr>
<td>YBCO</td>
<td>yttrium barium copper oxide</td>
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1

Introduction

Although efforts to make new materials, or to improve existing materials, are as old as mankind, ‘materials science’ has matured into a distinct discipline only since a few decades. In the earliest ages of civilization, materials were made by a learning-by-doing approach. The first piece of iron – which, apart from iron meteorites, does not occur in elemental form in nature – was most probably made by chance, when an iron ore and a carbon source were accidentally heated together. This was a quantum leap for mankind at the time of its discovery. ‘New materials’, with new chemical compositions and new morphologies, or materials with improved properties and better performances are still discovered today, but progress is essentially based on scientific and technological advances. For example, a detailed understanding of glass chemistry, the structure of glass, crystallization phenomena, the physics of melts, and so on paved the way from the first primitive man-made piece of glass to metallic glasses or the highest-quality optical glass used in the lenses of large telescopes. The development of ceramic materials from simple pottery, made from readily available raw materials, to today’s sophisticated functional ceramics for high-tech applications is routed on the same grounds.

In our generation, many new materials have been discovered with properties that were beyond imagination, such as the high-temperature superconductors, ‘intelligent’ and ‘adaptive’ materials, or nanostructured materials. Furthermore, the demand for longer product lifetimes, higher quality and efficiency, and so on has also placed new challenges on the synthesis and processing methods. An increasingly important goal for materials developments is the minimization of energy and raw materials consumption. When it comes to developing new materials with a targeted set of properties, the question is no longer solely whether such a material can be made, but whether it can be made with a minimal environmental impact. This includes the replacement of rare elements by more abundant ones.

In many areas, the rate of progress was and is determined by the speed at which materials are newly developed or improved. New materials enable new applications, and – vice versa – new applications require new materials. An example is information and communication technologies, ranging from mobile phones to computers, which have led to major changes in the way we live but would have not been possible without unprecedented developments in all
materials categories, ranging from polymers to semiconductors and alloys. ‘Those who control materials, control technology’ (E. Kobayashi, Panasonic). Technologies for renewable energy production and storage pose formidable new challenges to materials science and especially the development of new materials, likewise advances in medical technologies.

Many scientific and technological findings, together with a better understanding of the underlying basic chemical and physical principles, form the basis for new technologies in the twenty-first century. Several trends are apparent:

- Materials become increasingly specialized and multi-functional. In contrast to many traditional materials that have a broad range of applications, many modern materials are tailor-made for one special application.
- Certain functions are often only accessible by complex systems rather than individual compounds. Paying special attention to interfaces between the components of such systems is an issue of increasing importance.
- The borders between traditional materials types, such as ceramics, organic polymers, or ‘natural’ materials begin to disappear. New classes of materials are being developed that bridge the gaps between the traditional materials, such as inorganic–organic hybrid materials or biomimetic materials.
- It is realized that the transition between molecules and solids results in materials with unique physical or chemical properties. Nanomaterials have the potential of revolutionizing materials design for many applications.
- Computational methods have matured in a way that they are able to model materials on different length scales with ever greater detail and precision and even to predict materials properties.

Modern materials science is interdisciplinary and more than just a blend of some established areas, such as chemistry, physics or engineering. The complementary know-how and approaches from these disciplines are essential to carry materials developments from the raw materials to the final application. Suitable methods to produce a material with the desired composition and properties, including the selection of suitable starting compounds, are what chemists can contribute.

The triangle Synthesis and Processing–Composition and Structure–Properties and Performance represents the essential relations in materials science. Different structures and morphologies (on any length scale) influence the properties of a material with a given composition and depend to a very high degree on the way how the material was made or processed. Vice versa, certain applications require particular structural features and specific chemical compositions of the employed materials, which again require the deliberate choice of synthesis and processing procedures.

For example, SiO$_2$ can be crystallized as quartz (for oscillator crystals, for example) by hydrothermal treatment (Section 4.4.2). SiO$_2$ as a dense insulating layer in a microelectronic device would be made by chemical vapour deposition (Section 3.2.5.1). Biogenic processes produce amorphous silica, for example, as the aesthetically pleasing exoskeletons of diatoms (see Section 4.2.4.1). Silica with a high surface area, used as adsorbent or for thermally insulating materials, for example, is produced either by aerosol processes, where agglomerated
spherical, amorphous particles are obtained (see Section 3.3), or as aerogels with a highly porous network structure via sol–gel processing (see Section 4.5.7). Sol–gel processing also allows the preparation of amorphous SiO₂ powders or dense films. Porous silica spheres, prepared with the help of macromolecular templates, are used for targeted drug release (Section 7.3.3). Although the composition of all materials is SiO₂, completely different preparation routes are required. This example shows that many materials with a given chemical composition can be prepared by several methods. Organization of this book according to preparation processes thus has the inevitable consequence that some materials are treated in more than one chapter.

When does an inorganic compound qualify as a ‘material’, or in other words, how does this book differ from one on preparative inorganic chemistry? We do not attempt to define the term ‘material’, because many chemical compounds are potential materials, and thus the distinction is not always obvious. Not being too conservative, we considered materials as compounds that are utilized for some application or that have at least the potential for being used in such a manner. We will select representative examples to discuss the ways in which chemical compounds are transformed into materials and show both the options and problems that originate from the various preparation methods, independently of a particular chemical composition.
Solid-State Reactions

In this chapter, reactions will be discussed in which at least one of the reactants is in the solid state. A large variety of inorganic solids has been prepared by reacting a solid with another solid, a liquid (melt), or a gas, usually at high temperatures. We will first deal with reactions between two (or more) solid compounds (Section 2.1) followed by a section covering reactions between a solid and a gas (Section 2.2). No separate section is devoted to solid–liquid reactions, because in many reactions starting with solid compounds, a liquid phase (melt), sometimes even a gaseous compound, is formed at the reaction temperature, that is, many ‘solid–solid’ reactions are actually ‘solid–liquid’ reactions. It is sometimes difficult to determine what physical phases are involved in a given reaction. Fundamental processes during ceramics processing, especially sintering, during which powders are converted to dense solid bodies, are treated in Section 2.3. Section 2.4 describes intercalation reactions, in which guest species (atoms, ions, molecules, or even polymers) are inserted into a crystalline host lattice.

2.1 Reactions Between Solid Compounds

We will first discuss some general principles of reactions between two solids, which are often called the ‘ceramic method’ (Section 2.1.1). Reaction between solid compounds can be stimulated by applying mechanical forces; ‘mechanochemical syntheses’ are treated in Section 2.1.2. We will then turn to two important industrial processes, carbothermal reduction (Section 2.1.3) and combustion synthesis (Section 2.1.4).

2.1.1 Ceramic Method

The oldest and still most common method of preparing binary and multinary solid materials is by direct reaction of solid components at high temperatures. Since solids do not react with each other at room temperature — even if thermodynamics favours product formation — high temperatures are necessary to achieve appreciable reaction rates. The advantage of solid-state reactions is the ready availability of the precursors and the low cost for powder production on the industrial scale. There are, however, only limited possibilities for an in situ
monitoring of the progress of the reaction. Instead, physical measurements (such as X-ray diffraction) are periodically carried out. Because of this difficulty, mixtures of reactants and products are frequently obtained. Separation of the desired product from these mixtures is generally difficult, if not impossible.

We will not cover all the classes of compounds that can be prepared by solid–solid reactions. Rather, we will discuss some fundamental issues of this method after an introductory example.

An example. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) is (see Glossary) superconducting at about $-181 \, ^\circ\text{C}$ (‘high-temperature superconductor’), which is well above the temperature of liquid nitrogen (b.p. $-196 \, ^\circ\text{C}$) for cooling of the magnet. The unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Figure 2.1) is derived from the (see Glossary) perovskite structure.

Perovskites are a class of solid compounds of the general formula $\text{M}^{II}\text{M}^{IV}\text{O}_3$ with interesting electrical properties ([see Glossary] piezoelectricity, [see Glossary] ferroelectricity, or high-temperature superconductivity; Figure 2.2).

Figure 2.1 Deduction of the unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (right) from the (see Glossary) perovskite structure. Three perovskite unit cells (left) are stacked above each other. Then the oxygen atoms marked by an $x$ are removed.

Figure 2.2 In 1933, Walter Meissner and Robert Ochsenfeld discovered that a superconducting material will repel a magnetic field (the ‘Meissner–Ochsenfeld effect’). A body made of a superconducting material thus floats above the surface of a magnet.
The $M^{2+}$ and oxide ions occupy the anion sites of the rock salt structure, while the $M^{4+}$ ions are in one quarter of the octahedral sites (those only surrounded by oxide ions). YBa$_2$Cu$_3$O$_y$ is an oxygen-deficient variation of this structure type. Its unit cell (Figure 2.1) consists of three stacked perovskite unit cells with Ba$^{2+}$ and Y$^{3+}$ sharing the $M^{2+}$ positions and $\frac{2}{9}$ of the oxide ions removed for charge balancing (part of the copper is in the +II and part in the +III oxidation state). The critical temperature for superconductivity depends on the oxygen content $x$ of YBa$_2$Cu$_3$O$_{7-x}$. Only materials with $0 \leq x \leq 0.65$ are superconducting.

YBa$_2$Cu$_3$O$_7-x$ (YBCO) can be prepared by heating an intimate mixture of yttrium oxide (Y$_2$O$_3$), barium peroxide (BaO$_2$), and cupric oxide (CuO). The starting compounds should be fine-grained in order to maximize surface areas and hence reaction rates (see below). The powder is pressed to a pellet to ensure an intimate contact between the (see Glossary) grains. The pellets are placed in an alumina boat and heated in a furnace to 930 °C over a period of 8–12 hours, held at this temperature for 12–16 hours, allowed to cool to 500 °C, and held there for 12–16 hours. After heating to 930 °C, the composition is about YBa$_2$Cu$_3$O$_{6.5}$. By annealing the material at 500 °C, it reacts further with oxygen from the air, and the final composition is about YBa$_2$Cu$_3$O$_{6.9}$. The heating–cooling sequence is shown graphically in Figure 2.3. The oxygen content $x$ in YBa$_2$Cu$_3$O$_{7-x}$ depends very much on the oxygen partial pressure during annealing.

The annealing of YBa$_2$Cu$_3$O$_{6.5}$ in oxygen atmosphere to give superconducting YBa$_2$Cu$_3$O$_{6.9}$ is an example for a (see Glossary) topochemically controlled reaction, where reactivity is controlled by the crystal structure rather than by the chemical nature of the reactants.

Other precursor compounds may be employed for the synthesis of YBCO. For example, the metal trifluoroacetates are used for the preparation of YBCO films. Solutions of these salts are prepared by dissolving the metal oxides or metal acetates in trifluoroacetic acid (CF$_3$COOH). An intimate mixture of the metal oxides is obtained by slow heating of the metal trifluoroacetate mixture in moist air from 200 to 780 °C. Carbon dioxide (CO$_2$) and hydrofluoric acid (HF) are formed as gaseous by-products. The oxide mixture eventually reacts to give YBCO upon holding at 780 °C for one hour.

![Figure 2.3](image-url)  
**Figure 2.3** Heating protocol for the preparation of YBa$_2$Cu$_3$O$_{6.9}$ (see text).
Carbonates, nitrates, hydroxides, and other oxy salts that decompose at high temperatures are often employed in solid–solid reactions. The heating program depends very much on the form and reactivity of the reactants. In general, thermal decomposition of solids initiates at some structural defects such as surfaces, grain boundaries, or dislocations. The gaseous by-products have to diffuse out of the reaction mixture. If one or more of the reactants is an oxy salt, the mixture is heated first at an appropriate temperature for a few hours to allow decomposition to occur in a controlled manner. If this stage is omitted and the mixture is heated directly at a higher temperature, decomposition may occur very vigorously.

For solid-state reactions in general, some caution is necessary in choosing a suitable container material, which is chemically inert to the reactants at high temperatures. Platinum, silica, stabilized zirconia, and alumina containers are generally used for the synthesis of metal oxides, while graphite containers are employed for sulfides and other (see Glossary) chalcogenides or (see Glossary) pnictides. If one of the constituents is volatile or sensitive to the atmosphere, the reaction is carried out in sealed evacuated capsules.

2.1.1.1 General Aspects of Solid-State Reactions

For most solid-state reactions, it is usually incorrect and misleading to think in terms of reaction order, since the reactions do not involve molecules and the overall process may be controlled by various phenomena, such as nucleation, nuclei growth, diffusion of reactants, or the rate of the reaction at the phase boundary. The Avrami equation (Eq. (2.1) and Figure 2.4) describes how solids transform from one state of matter (phase) to another (such as crystallization, chemical reaction, phase transitions, and so on) at constant temperature. It represents the time-dependent volume fraction of the new phase \( x \) in the total system:

\[
x(t) = 1 - e^{kt^n}
\]

(2.1)

with \( 1 < n \leq 4 \) (\( n = 1 \) would correspond to a first-order reaction in molecular chemistry) and \( k \) the rate constant. For \( n > 1 \), the function has a sigmoid profile.

![Figure 2.4 Avrami equation for two different values of \( n \). The curve for \( n = 3 \) graphically shows the induction period at the beginning of the reaction. \( x \) is the volume fraction of the new phase in the total system.](image-url)
where the transformation rates are low at the beginning and the end of the transformation but rapid in between.

The initial slow rate can be attributed to the time required for a significant number of nuclei of the product phase to form and grow. Nucleation does not start everywhere simultaneously, but instead at a few locations. In the intermediate period transformation is rapid, because the growing nuclei consume the old phase while new nuclei continue to be formed. When the resulting product regions touch each other, the reaction rate starts to decrease again until no untransformed material remains. The process of (see Glossary) nucleation will be discussed in detail in Section 4.1.2. As a matter of fact, chemical reactions between two solids can only occur if the reactants are in intimate contact (see Section 2.1.1.2). This is an important difference to reactions between liquids, including solutions, and gases, where this is not an issue.

The nucleation step is easier if there is a structural similarity between the product and at least one of the reactants, because this reduces the degree of structural reorganization necessary for nucleation to occur. For instance, in the reaction of MgO and Al₂O₃, the oxide ion arrangement in the formed (see Glossary) spinel is similar to that in MgO (cubic close packing). Spinel nuclei may therefore form at the surface of the MgO crystals such that the oxide ion arrangement is essentially continuous across the MgO–spinel interface.

There are two types of oriented reactions: (see Glossary) epitactic and (see Glossary) topotactic reactions. In epitactic reactions, the structural relationship is restricted to the actual interface between the two crystals. For example, the two structures may have a common arrangement of oxide ions at the interface, but the structures at both sides of the interface may be different. Epitactic reactions therefore require only a two-dimensional structural similarity at the crystal interface. Topotactic reactions are more specific than epitactic ones because they require that a structural similarity continues into the bulk of both crystalline phases.

When nucleation is facilitated by a structural similarity, there is usually a clear orientation relationship between the structures of the reactant and product. Furthermore, the interatomic distances should be similar. Otherwise they cannot be matched over a large area of contact. For example, the oxygen–oxygen separation in MgO and BaO is quite different, although both compounds have the rock salt structure. A difference in interfacial lattice parameters of about 15% between nucleus and substrate is the most that can be tolerated for oriented nucleation.

The ease of nucleation of product phases also depends on the actual surface structure of the reacting phases. In most crystals the structure cannot be the same over the entire crystal surface. For example, the (100) planes of BaO contain Ba²⁺ and O²⁻ ions, while a (111) surface will be either a complete layer of Ba²⁺ ions or a complete layer of O²⁻ ions (Figure 2.5). Since different surfaces have different structures, their reactivity is likely to differ considerably. It is difficult, however, to give general rules about which surfaces are the most reactive. See also Section 4.2.2 for a discussion of surface energies.

From the above discussion it is clear that reaction between two solids may not occur even if thermodynamic considerations favour product formation. Apart from the area of contact between the reacting solids (see Section 2.1.1.2)
and the nucleation rate of the product phase, diffusion of ions through the various phases, especially through the product phase, influences the overall rate of reaction between solids.

In order to understand the difference between reactions in solution and in the solid state, and the problems associated with solid-state reactions, let us consider the thermal reaction of two crystals of the compounds A and B, which are in intimate contact across one face (Figure 2.6). When no melt is formed during the reaction, the reaction has to occur initially at the points of contact between A and B and later by diffusion of the constituents through the product phase.

The first stage of the reaction is the formation of nuclei of the product phase C at the interface between A and B. This may be difficult, if a high degree of structural
reorganization is necessary to form the product, as has been discussed before. After (see Glossary) nucleation of product C has occurred, a product layer is formed. At this stage, there are two reaction interfaces: one between A and C and another between C and B. In order for further reaction to occur, counter-diffusion of ions from A and B must occur through the existing product layer C to the new reaction interfaces.

As the reaction progresses, the product layer becomes thicker. This results in increasingly longer diffusion paths and slower reaction rates, because the product layer between the reacting particles acts as a barrier. In the simple case where the rate of the reaction is controlled by lattice diffusion through a planar layer, the rate law (Eq. (2.2)) has a parabolic form:

$$\frac{dx}{dt} = k \cdot x^{-1}$$

(2.2)

where $x$ is the amount of reaction (here equal to the thickness of the growing product layer), $t$ is time, and $k$ is the rate constant.

Ions are normally regarded as being trapped on their appropriate lattice sites, and it is difficult for them to move to adjacent sites. Only at very high temperatures do the ions have sufficient energy to diffuse through the crystal lattice. As a rule of thumb, two-thirds of the melting temperature of one component is sufficient to activate diffusion sufficiently and hence to enable the solid-state reaction. Diffusion of ions is also enhanced greatly by the presence and kind of crystal defects, especially vacancies and interstitials, but also occurs via structural defects such as dislocations and grain boundaries.

The formation of the (see Glossary) perovskite barium titanate ($\text{BaTiO}_3$) by solid-state reaction of $\text{BaCO}_3$ and $\text{TiO}_2$ may serve as an example. It also shows that such reactions are sometimes more complex. $\text{BaTiO}_3$ is an important material for the fabrication of thermistors, capacitors, optoelectronic devices, and DRAMs. $\text{BaO}$ (formed by decomposition of $\text{BaCO}_3$) has the rock salt structure (cubic close packing of the oxide ions; $\text{Ba}^{2+}$ ions in octahedral sites), while $\text{TiO}_2$ (rutile structure) has a hexagonal close packing of the oxide ions and $\text{Ti}^{4+}$ ions in half of the octahedral sites.

The formation of $\text{BaTiO}_3$ takes place in at least three stages:

1. First $\text{BaO}$ reacts with the outer surface regions of $\text{TiO}_2$ grains to form nuclei and a surface layer. This requires reorganization of the oxide lattice at the $\text{TiO}_2/\text{BaTiO}_3$ interface.
2. Further reaction of $\text{BaO}$ and the previously formed $\text{BaTiO}_3$ leads to the formation of the intermediate Ba-rich phase $\text{Ba}_2\text{TiO}_4$. The formation of this phase is necessary for the migration of the $\text{Ba}^{2+}$ ions.
3. $\text{Ba}^{2+}$ ions from the Ba-rich phase $\text{Ba}_2\text{TiO}_4$ migrate into the remaining $\text{TiO}_2$ to form $\text{BaTiO}_3$.

The discussion up to now has assumed that diffusion coefficients of phase A and B ions are equal. This is often not the case. Phenomena related to unequal flow of matter are commonly summarized as Kirkendall effect. If A diffuses faster into B than B into A, as schematically shown in Figure 2.7, the unequal flow of ions or atoms is balanced by vacancy (V) diffusion. Condensation of vacancies can give
rise to voids or even gaps at the interface between A and the product phase (AB) or deformations (or both). An example of Kirkendall voids is shown in Figure 2.8.

The Kirkendall effect normally has negative consequences, as it decreases the mechanical properties of interfaces or of adhesion and can cause wire bond failures in integrated circuits, for example. This can technically be avoided by introducing diffusion barrier layers. The Kirkendall effect has, however, recently received positive attention for the generation of hollow nanostructures (see Section 7.4.2). In a nutshell, if in a core–shell nanoparticle or nanotube (Section 8.5.1) the diffusion rate of the core material \( J_{\text{core}} \) is faster than that of the shell material \( J_{\text{shell}} \), voids form inside the nanoparticle, and their coalescence results in hollow structures.

### 2.1.1.2 Facilitating Solid-State Reactions

Apart from the problems arising from nucleation and diffusion, which are responsible for the high reaction temperatures and long reaction times, the ceramic method suffers from some other disadvantages. For example, in some systems the reaction temperature cannot be raised as high as necessary for reasonable reaction rates, because one or more components of the reacting...
mixture may volatilize, or the homogeneous distribution of dopants, important for many ceramic materials, is sometimes difficult to achieve. In order to overcome some of the problems, particularly to reduce the reaction times, it is necessary to optimize critical parameters.

**Contact area.** The surface area of a given amount of solid depends on the particle size. This is shown by a simple calculation. A cubic crystal with a volume of 1 cm$^3$ has six faces each with an area of 1 cm$^2$ and, therefore, a total surface area of 6 cm$^2$. When this crystal is now cut 10 times parallel to each face (Figure 2.9), $10^3$ cubic crystallites are obtained with a dimension of 0.1 $\times$ 0.1 $\times$ 0.1 cm each. The $10^3$ smaller cubes have the same mass and volume as the large cube, but their total surface area now is 10 times larger ($10^3 \times 6 \times 0.01$ cm$^2$).

Grinding of the 1 cm$^3$ crystal or ball milling for some time typically results in particles with an average size of about 10 $\mu$m ($10^{-3}$ cm). Hence, the total surface area of the powder would be $6 \times 10^3$ cm$^2$ (0.6 m$^2$) if all grains are cubic crystallites. Note that a 10 $\mu$m particle size still represents diffusion distances of about $10^4$ unit cells! The advantage of further decreasing the crystallite size in the nanometre range is obvious from these considerations. Solid-state reactions are often greatly facilitated by cooling and grinding the sample periodically. This is because sintering and grain growth of both reactant and product phases may occur during heating, causing a reduction in the surface area of the mixture. Grinding maintains a high surface area and brings fresh surfaces into contact.

Although the surface area of solids largely controls the area of contact between reacting (see Glossary) grains in a mixture, it does not appear directly in the equation for the rate of reaction, such as Eq. (2.2). However, it is included indirectly since there is an inverse correlation between the thickness of the product layer, $x$, and the area of contact. For example, when two cubic particles of 10 $\mu$m size react with each other, the product layer at 50% conversion is 10 $\mu$m thick. When the dimension of the crystals is decreased to 1 $\mu$m, the total surface area for a given mass of reactants is increased by a factor of 10 (see above), but the thickness of the product layer at 50% conversion is only 1 $\mu$m. According to Eq. (2.2), this will result in a faster reaction.

In practice, it is rather unlikely that all the surfaces of the reacting solids will be in intimate contact, and usually the contact area is considerably less than the
total surface area. The area of contact may be increased somewhat by pressing the reacting powder into a pellet. However, even at relatively high pressures, the crystal contacts are not maximized. A further increase in contact area and reduction in pellet porosity may be achieved by compressing the pellet at high temperatures, for example, by hot pressing. However, the densification process is usually slow and may require several hours.

**Facilitating diffusion.** Equation (2.2) relates the rate of solid-state reactions to the diffusion of ions through the bulk of the crystals and, especially, through the product phase. Diffusion path lengths are influenced, *inter alia*, by the particle size of the reactants, the degree of homogenization achieved during mixing, and the intimacy of contact between the (see Glossary) grains. Diffusion path lengths are greatly reduced when the cations are brought in close contact. To this end, solid compounds can be used that already contain the different cations in an ideally atomic dispersion. Such methods are mostly employed for the preparation of complex inorganic materials, such as ternary or quaternary oxides. The processing temperatures are generally lower, and the synthesis times shorter than in the classical ceramic method because of the high degree of homogenization and thus the shorter diffusion distances of the ions. Alternatively, solid-state reactions can be performed in molten fluxes or high-temperature solvents (such as Bi, Sn, halide salts, or alkaline metals).

**Co-precipitation.** Salts of the required metals are dissolved in the same medium (usually water) and co-precipitated either by concentrating the solution or by adding a precipitating reagent. The precipitate consists of an intimate mixture of two salts or a solid solution. Many mixed-metal hydroxides, carbonates, cyanides, oxalates, formates, or citrates can be co-precipitated, provided that the metal salts have similar solubility and precipitation rates or if (see Glossary) solid solutions are formed. The obtained precipitate is heated to the required temperature in a desired atmosphere to produce the final product. This may be illustrated by the synthesis of ZnFe$_2$O$_4$ (see Glossary) spinel (Eq. (2.3)). Oxalates of zinc and iron are dissolved in water in the ratio of 1:1. The solutions are then mixed and heated to evaporate the water. The precipitated fine powder is a solid solution that contains the cations mixed essentially on an atomic scale. The powder is filtered off and heated. The method has also been employed for the preparation of (see Glossary) superconducting YBa$_2$Cu$_3$O$_{7-x}$ and other complex oxides.

$$\text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{Zn}(\text{C}_2\text{O}_4) \rightarrow \text{ZnFe}_2\text{O}_4 + 4\text{CO} + 4\text{CO}_2$$ (2.3)

Another example is the formation of $\text{M}_{1-x}\text{M'}_x\text{O}$ ($\text{M} = \text{Ca, Mg, Mn, Fe, Co, Zn, Cd}$). Because their carbonates are isostructural (calcite structure), a large number of carbonate solid solutions $\text{M}_{1-x}\text{M'}_x(\text{CO}_3)$ containing two or more cations can be prepared. The carbonates are thermally decomposed in vacuum or in flowing dry nitrogen by cleavage of CO$_2$. The facile formation of the oxides $\text{M}_{1-x}\text{M'}_x\text{O}$ (rock salt structure) from the carbonates is due to the close relationship between the structures of calcite and rock salt.

Hydroxide solid solutions of the general formula $\text{Ln}_{1-x}\text{M}_x(\text{OH})_3$ ($\text{Ln} = \text{La or Nd}; \text{M} = \text{Al, Cr, Fe, Co or Ni}$) and $\text{La}_{1-x-\gamma}\text{Ni}_x\text{M}_y(\text{OH})_3$ ($\text{M} = \text{Co or Cu}$), crystallizing in the Ln(OH)$_3$ structure, were decomposed at relatively low temperatures (around 600°C) to yield LnNiO$_3$, LnNi$_{1-x}$Co$_x$O$_3$, LnNi$_{1-x}$Cu$_x$O$_3$, and so on.
2.1 Reactions Between Solid Compounds

A variation of the co-precipitation method is that stoichiometric mixed-metal salts are precipitated, where the cations are incorporated in the same solid precursor compound. For example, ferrite spinels such as NiFe$_2$O$_4$ can be prepared by slowly heating the mixed-metal acetate Ni$_3$Fe$_6$O$_3$(OH)(OAc)$_{17}$·2 py to 200–300 °C to burn off the organic material, followed by heating in air at ~1000 °C for two to three days. Another example is the synthesis of BaTiO$_3$ by thermal decomposition of the mixed oxalate Ba[TiO(C$_2$O$_4$)$_{1/2}$]. By careful control of the experimental conditions, these precursor methods are capable of yielding phases of accurate stoichiometry. In the given examples, the mixed-metal precursors decompose without change of the oxidation state of the involved elements. Mixed-metal precursors decomposing through redox reactions are also possible; this is treated in Section 2.1.4.1.

**Gel methods.** In solution, the ions of dissolved salts are randomly distributed. If the solution is converted into a (see Glossary) gel, this random distribution is kind of 'trapped', and ions of different metals are mixed at an atomic scale. Upon heating of the gels, the gel matrix is pyrolysed and an inorganic solid is obtained. The final material is obtained at considerably lower temperatures compared with the ceramic method where mass transport between the grains limits the reaction. Mixed-metal gels can be obtained by sol–gel processing, where gels are formed by hydrolysis and condensation reactions (see Section 4.5). Alternative methods have been developed that can employ aqueous solutions of metal salts for the synthesis of metal oxides or ceramic structures.

Citric acid (Eq. (2.4)) is a compound capable of forming stable metal complexes with nearly all metal ions (except monovalent ions such as Na$^+$ or K$^+$). The complexes have a wide variety of compositions and structures. Citrate (see Glossary) ligands can occupy up to four coordination sites after deprotonation of the alcoholic C–OH and the three carboxylate groups of citric acid, and they can coordinate to the same metal or bridge different metals. In [Cu$_2$(citrate)$_2$]$^{4-}$ as an (arbitrarily chosen) example (Eq. (2.4)), the citrate ligands are both (see Glossary) chelating and bridging, while one COO$^-$ group of each citrate ligand is dangling and thus available for further reactions.

When one or more metal salts are mixed with citric acid and heated, viscous solutions/gels are formed. Ammonia or amines are sometimes added to bind the dissociated protons. The easy formation of gels is due to the many coordination possibilities of citrate ligands, including the ability to bridge different metals. Conversion of the gel to a metal oxide is simply achieved by (see Glossary) pyrolysis in air, with the maximum temperature depending on the system.
The ‘citrate–gel’ method is a versatile method for the preparation of (nanosized) binary and multinary metal oxides. The presence of the organic matrix in the early stages of the pyrolysis reaction ensures that nucleation occurs simultaneously at many sites, resulting in small crystallite sizes. When metal nitrates are employed, the reaction can be self-sustaining, with nitrate as the oxidant and citrate as the fuel (see Section 2.1.4.1).

The so-called Pechini method goes a step further by combining metal complex formation and in situ (see Glossary) polymerization of organic compounds. A typical Pechini procedure involves dissolution of metal salts in ethylene glycol that contains citric acid. Citric acid has a twofold role as it forms stable citrate complexes (Eq. (2.4)) and also results in the formation of polymers by esterification with ethylene glycol (linkage as in polyesters). One of the advantages of the Pechini method is that the viscosity of the polymeric resin can be tailored by the citric acid/ethylene glycol ratio. The polymer matrix is removed by subsequent heating of the resin, typically to 500–1000°C, and products with good homogeneity are obtained. For example, small amounts of well-dispersed dopants can easily be introduced in the final material, simply by dissolving the necessary portion of the corresponding metal salts in the starting solution. Citric acid can be replaced by other di-, tri-, or tetra-carboxylic acids, and ethylene glycol by other polyols. Compared with the citrate–gel method, the thermal decomposition of the organic matrix is delayed, which allows a better control of the properties of the obtained powders. If metal nitrates are used as precursors, the Pechini method would involve a combustion reaction during the final heating step.

Apart from powders, ceramic films and coatings can also be obtained. To this end, an aqueous or alcoholic solution of the metal salt(s), citric acid, and ethylene glycol is coated on a solid substrate and then heated.

### 2.1.2 Mechanochemical Synthesis

Mechanochemistry studies chemical and physicochemical processes stimulated or accelerated by mechanical activation of solids, such as compression, shear, or friction. In mechanochemical processes, the required energy is provided by mechanical force, similar to thermo-, photo-, or electrochemistry, where energy is provided by heat, radiation, or electric potential. In a typical procedure, fine-grained powders are placed together with a number of hardened steel or tungsten carbide (WC)-coated balls in a sealed container, which is vigorously agitated at room temperature, mainly in planetary mills.

As discussed above, reactions between two solids involve the formation of a product phase at the interfaces of the reactants followed by diffusion of atoms of the reactant phases through the product phase (Figure 2.6). High temperatures are therefore required for the reaction to occur at reasonable speeds. In contrast, an excess of free energy is produced mainly by elastic and plastic deformation arising under the joint action of high pressure and shear, and active surfaces of solids are formed by friction and fracture. Mechanical activation generates clean and fresh surfaces, induces grain boundary disordering, increases defect density, and reduces particle sizes (increasing the contact area between particles). Diffusion of atoms is thus substantially accelerated, and therefore the reaction
2.1 Reactions Between Solid Compounds

rates increase even at ambient temperatures. Although part of the mechanical energy is transformed to heat and, consequently, temperature can locally increase, overall temperature changes play no significant role in the majority of mechanochemical reactions. For example, synthesis of zinc ferrite, \( \text{ZnFe}_2\text{O}_4 \), from \( \text{Fe}_2\text{O}_3 \) and \( \text{ZnO} \) requires heating to 800 °C for two hours for quantitative reaction. The same result can be achieved within the same period by ball milling at room temperature.

During mechanical attrition the powder particles are subjected to severe mechanical deformation from collisions with the hard balls. The deformation is localized at the early stage in shear bands, with a thickness of about 1 μm, extending throughout the entire particle and consisting of series of high-density dislocations. Nanometre-sized grains are nucleated within these shear bands. This results in an extremely fine-grained microstructure with randomly oriented grains separated by high-angle grain boundaries for longer duration of ball milling.

One of the advantages of mechanochemical synthesis is that solids can be obtained from components with large differences in melting points or between melting and boiling points. For example, the boiling point of silicon (3265 °C) is below the melting point of tungsten (3414 °C), and the densities differ by a factor of more than 8 (2.31 and 19.35 g cm\(^{-3}\), respectively). This renders preparation of monophase tungsten silicides by standard methods very difficult, while mechanochemical synthesis is possible.

Mechanochemistry offers many possibilities for low-temperature reactions in the solid phase without dissolution or melting of reagents. When mechanochemical reactions are conducted in air, oxide materials are usually obtained. If the mechanochemical device is filled with an inert gas, non-oxide materials can be prepared as well. One of the prominent features of mechanochemical processes is homogeneous dispersion and mixture of different components. Such processes are therefore very suitable for the preparation of (see Glossary) composite materials or supersaturated solid solutions.

Mechanochemical synthesis is not only restricted to inorganic materials, such as metal oxides, (see Glossary) refractory compounds, intermetallic compounds, or mixed-metal halides. In many cases, nanocrystalline materials are obtained. Organic compounds, metal complexes, polymers, or pharmaceutical preparations can be prepared as well. For example, the first mechanochemical synthesis of a metal–organic framework (MOF) (see Section 6.2) was achieved by simply grinding copper acetate and isonicotinic acid. The highly crystalline compound \( \text{Cu}(\text{isonicotinate})_2 \) was obtained as a single product in only 10 minutes without heating. Many more MOFs have been prepared similarly meanwhile.

While mechanochemical syntheses are cost effective and reproducible and require no solvent, the relatively poor controllability over the reaction conditions and a lack of understanding of the systems are on the negative side.

2.1.3 Carbothermal Reduction

Carbothermal reduction is practised commercially for the synthesis of many non-oxide ceramic powders such as carbides, nitrides, or borides.
We will discuss this method for one of the most prominent carbothermal reduction processes, the so-called Acheson process. Almost all silicon carbide, SiC (‘carborundum’), produced worldwide is made by this method. SiC is mainly used in four areas of application:

- For cutting and grinding precious and semi-precious stones and for fine grinding and lapping of metals and optical glasses. Bound with synthetic resins and ceramic binders, SiC grits are used in grinding wheels, whetstones, hones, abrasive cutting-off wheels, and monofiles for machining of all types of materials.
- In cast iron and steel production as a deoxidant and for carburization and siliconization.
- As a structural (see Glossary) refractory material with excellent thermal shock, oxidation, and corrosion resistance in linings and skid rails for furnaces and in kiln furniture.
- As electric heating elements and electrical resistors. For example, SiC is used for heating elements operating in oxidizing atmospheres up to 1500 °C owing to its good electric conductivity combined with its excellent oxidation resistance.

The first commercial plant to produce SiC was built in 1896 in Niagara by Acheson to meet the demand for abrasives at this time. The basic design of the original electric furnace (Figure 2.10) has remained unchanged, despite larger sizes and better efficiency. Most Acheson furnaces are shaped like a trough.

**Figure 2.10** Section through an Acheson furnace before (a) and after the reaction (b).
Graphite electrodes connected to a graphite core (that constitutes the initial electrical path through the reaction mixture) are laid in a mixture of carbon and sand. When an electric current is passed through the graphite core, the charge is heated from within by resistive heating. The reaction takes place at temperatures above 1577 °C. This results in the formation of a hollow cylinder of SiC and the expulsion of carbon monoxide gas. The charge acts as a refractory container as well as a thermal insulator for the ingot being formed.

Current conventional furnaces are about 12–18 m long, and the power intensities approach 260 kW m$^{-1}$. The technological limit to furnace size and power intensity is the available electrical power supply technology. The manufacture of 1 kg SiC requires about 12 kWh; most plants are therefore located in areas where power is relatively inexpensive.

The overall reaction of the SiC formation is

$$\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO} \quad (2.5)$$

The SiO$_2$ source can be sand, quartzite, or crystalline rock quartz. The most common carbon source is petroleum coke, the final residue from crude oil refining. Carbon black, graphite, charcoal, pyrolysed organic polymers, or other carbon sources can also be used. The particle size of both components is in the range of 5–10 mm; the size distribution should be narrow so that the final furnace mix is permeable to the CO gas that must leave the reaction zone. Porosity agents, such as sawdust, bagasse, or rice hulls, are often incorporated into the furnace mix to make it additionally permeable to the escaping CO. High pressures of gas may locally build up to form voids and channels to more porous parts of the mixture. The product from an Acheson furnace at the end of a run is a large hollow cylinder (Figure 2.10). The unreacted furnace mix is recycled.

Pure SiC is colourless and transparent. However, such pure SiC cannot be made by the Acheson process because nitrogen from the air is soluble in SiC, causing the crystals to take a green colour. Black SiC is obtained in the presence of impurities, such as Al (maximum solubility 2%) and B (maximum solubility 0.5%). To make green SiC, the furnace mixture must be made from quartz and low metal content coke. The highest tonnage application for SiC (about 50% of the produced SiC) is ‘metallurgical SiC’, a silicon and carbon source for the iron casting industry, where purity is not important. Purer SiC is needed for abrasive (about 40%), refractory, and other applications.

The SiC-forming reaction is much more complicated than given in Eq. (2.5). Originally, it was assumed that SiC solely results from solid-state reaction between SiO$_2$ and carbon. However, this is not reasonable for the relatively large particle sizes used in commercial SiC production. One of the current models is that SiC forms as a result of four sub-reactions (Eqs. (2.6)–(2.9)), which provide mass transport via the vapour phase.

$$\text{SiO}_2(s) + \text{C}(s) \rightarrow \text{SiO}(g) + \text{CO}(g) \quad (2.6)$$

$$\text{SiO}_2(s) + \text{CO}(g) \rightarrow \text{SiO}(g) + \text{CO}_2(g) \quad (2.7)$$

$$\text{C}(s) + \text{CO}_2(g) \rightarrow 2\text{CO}(g) \quad (2.8)$$

$$2\text{C}(s) + \text{SiO}(g) \rightarrow \text{SiC} + \text{CO}(g) \quad (2.9)$$
SiO₂ initially reacts at the contact points with coke particles in a solid-state reaction to liberate CO and gaseous SiO (Eq. (2.6)). Reaction of the CO with more SiO₂ results in the formation of additional SiO and CO₂ (Eq. (2.7)). Carbon dioxide is reconverted to CO by the Boudouard equilibrium (Eq. (2.8)). SiC is formed by reaction of gaseous SiO directly at the surface of the carbon particles once the C/SiO₂ contact points are consumed (Eq. (2.9)). Silicon is transported to the carbon particles in the form of SiO (Figure 2.11). As the product layer grows, the reaction surface decreases and the reaction gets slower.

Porous (cellular) SiC can also be produced by this method. Native wood is converted into carbon preforms by high-temperature (see Glossary) pyrolysis in an argon atmosphere. Subsequent infiltration and reaction with gaseous SiO at 1600 °C results in a biomorphic SiC ceramic (see also Section 3.2.7 on chemical vapour infiltration). The pore structure of the SiC ceramic reproduces the original wood morphology, as shown in Figure 2.12.

Carbides are made by the high-temperature reaction between carbon and metal oxides alone, as discussed for the Acheson process above. The synthesis of borides requires the presence of elemental boron that is usually formed in situ by reduction of B₂O₃. The required energy (with B₂O₃ as the boron source) is greater than for the corresponding carbides because carbon has to reduce both the metal oxide and B₂O₃. Nitrides are obtained in the presence of nitrogen sources, usually elemental nitrogen (‘carbothermal nitridation’). In all cases, the reactions are

Figure 2.11 Material transport paths during the preparation of SiC by the Acheson process.

Figure 2.12 Cellular microstructure of native tissue oak (a), the carbon preform obtained by pyrolysis (b), and biomorphic SiC ceramic after reaction with SiO at 1600 °C (c).
Table 2.1 Examples for the carbothermal reduction and minimum temperatures.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Minimum temperatures (°C) at atmospheric pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbides</strong></td>
<td></td>
</tr>
<tr>
<td>$2\text{Al}_2\text{O}_3 + 9\text{C} \rightarrow \text{Al}_4\text{C}_3 + 6\text{CO}$</td>
<td>1950</td>
</tr>
<tr>
<td>$2\text{B}_2\text{O}_3 + 7\text{C} \rightarrow \text{B}_4\text{C} + 6\text{CO}$</td>
<td>1550</td>
</tr>
<tr>
<td>$\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$</td>
<td>1500</td>
</tr>
<tr>
<td>$\text{TiO}_2 + 3\text{C} \rightarrow \text{TiC} + 2\text{CO}$</td>
<td>1300</td>
</tr>
<tr>
<td>$\text{WO}_3 + 4\text{C} \rightarrow \text{WC} + 3\text{CO}$</td>
<td>700</td>
</tr>
<tr>
<td>$2\text{MoO}_3 + 7\text{C} \rightarrow \text{Mo}_2\text{C} + 6\text{CO}$</td>
<td>500</td>
</tr>
<tr>
<td><strong>Borides</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3 + 12\text{B}_2\text{O}_3 + 39\text{C} \rightarrow 2\text{AlB}_12 + 39\text{CO}$</td>
<td>1550</td>
</tr>
<tr>
<td>$\text{V}_2\text{O}_5 + \text{B}_2\text{O}_3 + 8\text{C} \rightarrow 2\text{VB} + 8\text{CO}$</td>
<td>950</td>
</tr>
<tr>
<td>$\text{V}_2\text{O}_3 + 2\text{B}_2\text{O}_3 + 9\text{C} \rightarrow 2\text{VB}_2 + 9\text{CO}$</td>
<td>1300</td>
</tr>
<tr>
<td>$\text{TiO}_2 + \text{B}_2\text{O}_3 + 5\text{C} \rightarrow \text{TiB}_2 + 5\text{CO}$</td>
<td>1300</td>
</tr>
<tr>
<td>$2\text{TiO}_2 + \text{B}_4\text{C} + 3\text{C} \rightarrow 2\text{TiB}_2 + 4\text{CO}$</td>
<td>1000</td>
</tr>
<tr>
<td><strong>Nitrides</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO}$</td>
<td>1700</td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{BN} + 3\text{CO}$</td>
<td>1000</td>
</tr>
<tr>
<td>$3\text{SiO}_2 + 6\text{C} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4 + 6\text{CO}$</td>
<td>1550</td>
</tr>
<tr>
<td>$2\text{TiO}_2 + 4\text{C} + \text{N}_2 \rightarrow 2\text{TiN} + 4\text{CO}$</td>
<td>1200</td>
</tr>
<tr>
<td>$\text{V}_2\text{O}_5 + 5\text{C} + \text{N}_2 \rightarrow 2\text{VN} + 5\text{CO}$</td>
<td>600</td>
</tr>
</tbody>
</table>

highly exothermic and thermodynamically favourable at very high temperatures. Since the reactions are reversible, it is advantageous to remove the by-product CO. Selected examples are shown in Table 2.1.

The fact that many of the carbothermal reductions are intrinsically fast is evidence that solid–solid reactions do not dominate the process. As for the Acheson process, gaseous species play a very important role. Some of the solid reactant metal oxides sublime, have a substantial vapour pressure, dissociate, or are reacted into volatile species within the temperature range for reaction.

Reduction processes involving CO are believed to be the primary route for the reduction of certain oxides to produce gaseous suboxides. Carbothermal reductions involving $\text{SiO}_2$ almost always occur through gaseous $\text{SiO}$, as already discussed (Eqs. (2.6) and (2.7)). Under reducing conditions, $\text{SiO}$ is the dominant gaseous species at temperatures between about 1000 and 1700°C. Other examples for the formation of suboxides by CO are given in Eqs. (2.10) and (2.11).

$$\text{B}_2\text{O}_3 + \text{CO} \rightarrow \text{B}_2\text{O}_2(\text{g}) + \text{CO}_2 \quad \text{(2.10)}$$

$$\text{Al}_2\text{O}_3 + 2\text{CO} \rightarrow \text{Al}_2\text{O}(\text{g}) + 2\text{CO}_2 \quad \text{(2.11)}$$
In carbothermal reductions involving $\text{B}_2\text{O}_3$, there is an increasing vapour pressure of $\text{B}_2\text{O}_3$ at temperatures above the melting point of $450^\circ\text{C}$. At $T \gtrsim 1450^\circ\text{C}$, $\text{B}_2\text{O}_2$ (and other B/O species) are becoming more important. For $\text{Al}_2\text{O}_3$ systems under reducing conditions, the major gaseous aluminium species above $1200^\circ\text{C}$ are gaseous Al and $\text{Al}_2\text{O}_3$. Reaction of the suboxides ($\text{B}_2\text{O}_2$ or $\text{Al}_2\text{O}$) with solid carbon provides a mechanism for the formation of the carbides similar to Eq. (2.9).

Liquid phases (melts) may also be involved, particularly for reactions with $\text{B}_2\text{O}_3$. During the formation of $\text{B}_4\text{C}$, there is a change in mechanism at $T \approx 1700^\circ\text{C}$. The liquid-phase reduction of $\text{B}_2\text{O}_3$ (Eq. (2.12)) dominates at lower temperatures, and the gas-phase reaction at higher temperatures (Eq. (2.13)).

\begin{align*}
7\text{C}(s) + 2\text{B}_2\text{O}_3(l) & \rightarrow \text{B}_4\text{C}(s) + 6\text{CO}(g) \quad (2.12) \\
5\text{C}(s) + 2\text{B}_2\text{O}_2(g) & \rightarrow \text{B}_4\text{C}(s) + 4\text{CO}(g) \quad (2.13)
\end{align*}

In the carbothermal nitridation of silicon, $\text{Si}_3\text{N}_4$ can be formed from $\text{SiO}$ either by reaction with solid carbon (Eq. (2.14)) or by reaction with CO in a gas-phase reaction (Eq. (2.15)).

\begin{align*}
3\text{C} + 3\text{SiO} + 2\text{N}_2 & \rightarrow \text{Si}_3\text{N}_4 + 3\text{CO} \quad (2.14) \\
3\text{CO} + 3\text{SiO} + 2\text{N}_2 & \rightarrow \text{Si}_3\text{N}_4 + 3\text{CO}_2 \quad (2.15)
\end{align*}

In general, the manufacture of non-oxide ceramic materials by carbothermal reduction can be carried out in a variety of ways, and various types of reactors have been developed (electric arc furnaces, moving bed furnaces, rotary tube reactors, fluidized bed reactors, and so on). A discussion of the advantages and disadvantages of the various reactor types would be beyond the scope of this book.

Although the final equilibrium products are determined solely by the temperature, pressure, and chemical species present, the mechanism and rate of a given reaction depend on a number of additional variables, such as particle size, degree of mixing of the reactants, diffusion rates, gas concentration, porosity, and the presence of impurities, as already discussed in Section 2.1.1.

### 2.1.4 Combustion Synthesis

In classical solid-state reactions (ceramic method; see Section 2.1.1), the reactants have to be heated continuously until they are completely converted into the product phase. In contrast, combustion syntheses, or ‘self-propagating high-temperature syntheses’ (SHS), exploit highly exothermic reactions. Such reactions typically have high activation energies. Once the reactions are initiated by energy input from an external source, sufficient heat is released to render the reactions self-sustaining. The reactants are thus heated rapidly ($10^3$–$10^6 \text{ K s}^{-1}$) to very high temperatures. The reactions are so fast that they are pseudo-adiabatic, that is, all the energy produced by the exothermic reaction is used to heat the sample. For example, reaction of Ti and C (Eq. (2.16)) liberates $183 \text{ kJ mol}^{-1}$. 

\begin{align*}
\text{Ti} + 3\text{C} & \rightarrow \text{Ti}_3\text{C} + 3\text{CO} \quad (2.16)
\end{align*}