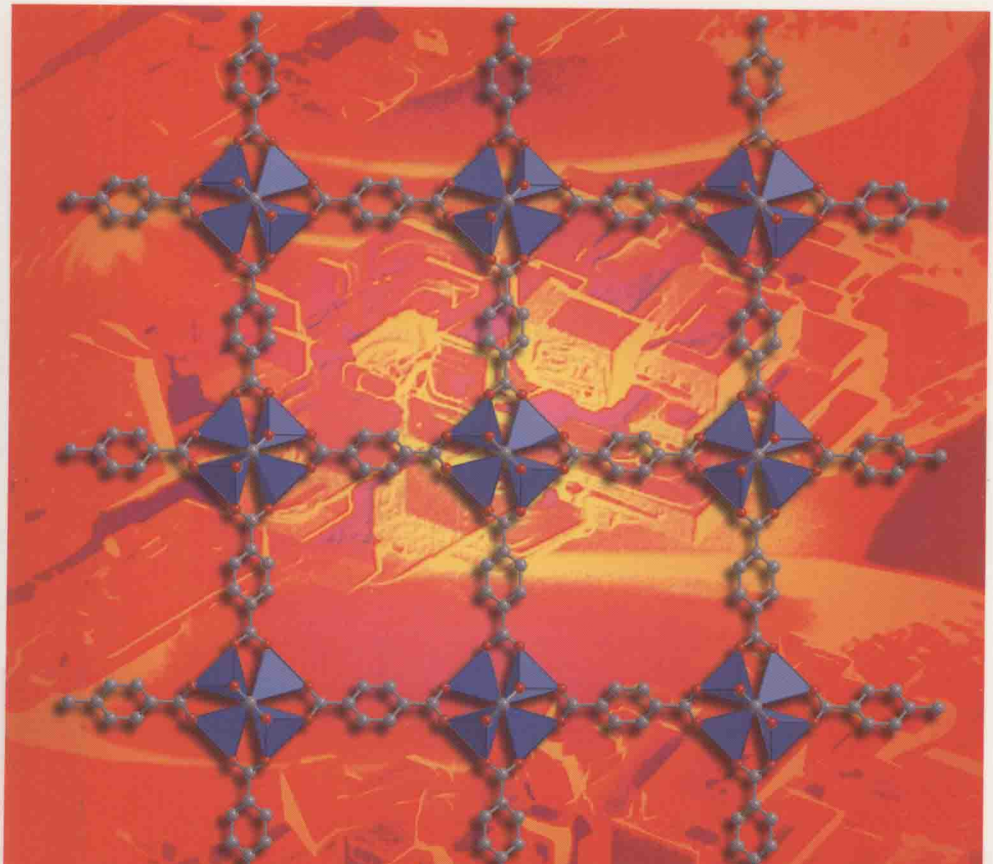
Ulrich Schubert, Nicola Hüsing

WILEY-VCH

# Synthesis of Inorganic Materials

Second, Revised and Updated Edition



Ulrich Schubert, Nicola Hüsing

# Synthesis of Inorganic Materials

Second, revised and updated edition

WILEY-VCH

WILEY-VCH Verlag GmbH & Co. KGaA

Prof. Dr. Ulrich Schubert
Institute for Materials Chemistry
Vienna University of Technology
Getreidemarkt 9/165
A-1060 Wien
Austria

Prof. Dr. Nicola Hüsing
Inorganic Chemistry I
University of Ulm
Albert-Einstein-Allee 11
D-89069 Ulm
Germany



Library of Congress Card No. applied for.

British Library Cataloguing-in-Publication Data: A catalogue record for this book is available from the British Library

Bibliographic information published by Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <http://dnb.ddb.de>

ISBN 3-527-31037-1



Printed on acid-free paper.



Printing: Strauss GmbH, Mörlenbach
Bookbinding: J. Schäffer GmbH i. G. Industrie- und Verlagsbuchbinderei, Grünstadt
Cover illustration: Gunther Schulz, Fußgönheim

Printed in the Federal Republic of Germany.

U. Schubert, N. Hüsing

# Synthesis of Inorganic Materials

Further Titles of Interest:

**M. Koehler, W. Fritzsche**
Nanotechnology
An Introduction to Nanostructuring Techniques

2004, ISBN: 3-527-30750-8

**P. Jutzi, U. Schubert (Eds.)**
Silicon Chemistry
From the Atom to Extended Systems

2003, ISBN: 3-527-30647-1

**G. Meyer, D. Naumann, L. Wesemann (Eds.)**
Inorganic Chemistry Highlights

2002, ISBN: 3-527-30265-4

**G. Meyer, D. Naumann, L. Wesemann (Eds.)**
Inorganic Chemistry Highlights II

2005, ISBN: 3-527-30811-3

## Preface to the Second Edition

When the first edition of this book was published in 2000, we hoped that the book would make the role of chemistry in materials science more visible, especially to students, and provide an overview of chemical methods for the synthesis of inorganic materials. The success of the first edition encouraged us to revise and update the book, and we are grateful for the very positive feedback.

In this 2nd edition, two chapters – Chapter 6 on porous materials and Chapter 7 on nanostructured materials – have been completely re-written and re-organized, mainly because of the rapid developments in these areas. We have added new sub-chapters, for example on nanotubes and metal-organic frameworks, new figures and new examples, such as biomorphous ceramics and light-emitting diodes. Some sections now have a new focus, while the recommended literature has been updated.

We hope that the second edition will continue to bridge the gap between fundamental and applied science, and between the various disciplines in materials science.

Vienna, August 2004

Nicola Hüsing
Ulrich Schubert

## Foreword

Within a textbook, there are several possible ways in which materials may be treated, according to:

- their chemical composition (organic polymers, metals, oxides, nitrides, carbides, etc.);
- their physical state (ceramics, glass, composites, polymers, etc.);
- their properties and applications (electronic materials, magnetic materials, optical materials, etc.);
- technological aspects (powder preparation, sintering methods, preparation of films or coatings, etc.); and
- the methods for their preparation (solid state reactions, polycondensations, gas phase reactions, etc.).

In most materials science and solid state chemistry textbooks – even those that are highly recommended ones – there is a regrettable lack of chemical information. Materials science is often reduced to physical and technological aspects, and chemistry is only introduced to discuss bonding and to describe structures. Processes for the preparation and modification of materials – the most important contribution of chemistry to material science – 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 a lecture course on "Inorganic materials from molecular precursors" given by the authors at the Vienna University of Technology. The selection of suitable precursors and the development of correct conditions to obtain a product with the desired composition and properties and a suitable (micro-) structure is what chemists can contribute to materials science.

Nevertheless, 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 at the end of the book may help to bridge the gap between chemical/physical/materials science fundamentals.

In an up-to-date textbook, SI units should be used exclusively. However, different scientific communities still have their own habits concerning physical units (e.g., 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.

Since the main focus of this book is on syntheses, we did not treat all major inorganic materials comprehensively, neither did we discuss naturally occurring materials such as lime, asbestos, gypsum, etc. Instead, some materials were selected as 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.

The book is organized according to preparation processes. Since many materials can be prepared using several methods, this organization inevitably has the consequence that some materials are treated in more than one chapter. For example, perovskites can be prepared by solid state reactions, by sol–gel processing, by hydrothermal processes, or by CVD, and is therefore discussed in different chapters.

One difficulty we were facing was to avoid writing a textbook on preparative inorganic chemistry, i.e., to discuss the preparation of inorganic *materials* instead of inorganic *compounds*. In fact, almost any chemical compound is a potential "material", and therefore the distinction is not always obvious. Not being too conservative, we considered materials as compounds that are used technically, or which have the potential for being used. In order to stay as close as possible to the real world of material science, we have tried to introduce a relevant technically applied material in most sub-chapters. The properties and uses of this material are discussed exemplarily.

At the end of each chapter, a selection of more recent books and review articles is provided, which may help the reader to study those processes under discussion in greater detail.

## Acknowledgements

We thank Harald Schauer who made invaluable contributions to this book with his careful and patient drawing of the majority of figures.

We thank the following companies and institutions who have provided us with information on, and photographs of, their products that allowed us to illustrate the technical relevance of the methods discussed:

- *Agfa-Gevaert*, Leverkusen (Dr. Wolfgang Schmidt), on the preparation of silver halides for photographic emulsions (Figure 4-15),
- *Austria Microsysteme Intl.*, Unterpremstätten (Dr. Holger Wille), on CVD processes for microelectronics (Figure 3-15),
- *Degussa*, Hanau, on the Aerosil process (Figures 3-27, 3-28, and 3-29),
- *Department of Materials Science, University of Erlangen-Nürnberg* (Prof. Dr. Peter Greil) on biomorphic SiC ceramics (Figure 2-10),
- *ESK*, Kempten (Dr. Karl A. Schwetz), on the preparation of silicon carbide by carbothermal reduction.
- *Fraunhofer-Institut für Silicatforschung*, Würzburg (Dieter Sporn and Dr. Klaus Rose) on sol–gel materials (Figures 4-44, 4-45, 4-63, and 4-65),
- *Hoechst AG*, Frankfurt, on aerogels (Figure 6-15),
- *Institut für Anorganische Technologie, Vienna University of Technology* (Prof. Dr. Benno Lux and Dr. Roland Haubner) on diamond films (Figure 3-20),
- *Philips Forschungslaboratorien*, Aachen (Dr. Ulrich Nieman), on halogen lamps (Figure 3-3),
- *Wacker-Chemie*, Burghausen (Dr. Johann Weis), on silicones (Figures 5-4 and 5-5).

The following publishers transferred copyrights for the reproduction of figures from their publications:

*Academic Press:* C. J. Brinker, G. W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol-Gel-Processing*: Figures 4-17, 4-42, 4-47 and 4-52.

*American Chemical Society, Chemistry of Materials*: Figure 2-23 (*10*, **1998**, 2898), Figure 2-27 (*8*, **1996**, 1752), Figure 4-18 (*4*, **1992**, 549), and Figure 6-32 (*8*, **1996**, 1682);
*Journal of Chemical Physics*: Figure 7-6 (*98*, **1994**, 7665);
*Advances in Chemistry, Series*: Figure 4-29 (*245*, **1995**, 535).

*Chapman & Hall:* A. W. Weimer (Ed.), *Carbide, Nitride and Boride Materials - Synthesis and Processing*: Figures 2-9, 2-19 and 3-5.

*CRC Press: Handbook of Optical Properties Vol. II*: Figure 7-8.
*Elsevier: Aerosol Science and Technology*: Figure 3-32 and 3-33 (*19*, **1993**, 434), Figure 7-3 (*19*, **1993**, 416);
*Chemical Physics Letters*: Figure 7-10 (*321*, **2000**, 163);
*Endeavour*: Figure 4-38 and 4-39 (**1969**, 114);
*Microelectronic Engineering*: Figure 4-43 (*29*, **1995**, 161);
*Microporous Mesoporous Materials*: Figure 6-38 and 6-39 (*44-45*, **2001**, 227);
*Thermochimica Acta*: Figure 3-4 (*299*, **1997**, 50).
*Gordon and Breach Publishers:* B. Marciniec, J. Chojnowski (Eds.), *Progress in Organosilicon Chemistry*: Figure 5-6.
*Harry Deutsch Verlag:* K. T. Wilke, *Kristallzüchtung*: Figure 4-37.
*International Union of Pure and Applied Chemistry: Pure Appl. Chem.*: Figure 6-24 (*73*, **2001**, 381).
*Institute of Electrical and Electronics Engineers: IEEE J. on Selected Topics in Quantum Electronics:* Figure 3-25 (*8*, **2002**, 264).
*Kluwer: Journal of Materials Science*: Figure 6-6 (*18*, **1983**, 1899).
*Materials Research Society: Journal of Materials Research:* Figure 7-2 (*9*, **1994**, 1307);
*MRS Bulletin:* Figure 3-6 (*18*(6), **1993**, 25), Figures 6-1 and 6-11 (*14*(4), **1994**, 24), Figure 6-4 (*14*(4), **1994**, 15).
*Nature Publishing Group (Nature)*: Figure 6-31 (*402*, **1999**, 278).
*Pergamon Press:* C. Suryanarayana, *Non-Equilibrium Processing of Materials*: Figure 4-11, 4-12 and 4-13.
*Current Opinion in Solid State & Materials Science*: Figure 3-12 (*3*, **1998**, 147), Figure 6-34 (*1*, **1996**, 798).
*Progress in Materials Science*: Figure 2-11 (*37*, **1993**, 123).
*Progress in Solid State Chemistry:* Figure 2-20 (*19*, **1989,** 28);
*The Royal Society of Chemistry:* J. E. Shelby, *Introduction to Glass Science and Technology*: Figure 4-1;
*Chemical Society Reviews:* Figure 6-27 (*32*, **2003**, 276).
*Springer: Marine Biology*: Figure 4-21 (*19*, **1973**, 323).
*van Nostrand Reinhold:* R. Szostak, *Molecular Sieves – Principles of Synthesis and Identification*: Catalysis Series, **1989**, Figures 6-21, 6-23, 6-25 and 6-26.
*VEB-Verlag Leipzig:* A. Petzold, *Anorganisch-nichtmetallische Werkstoffe*: Figure 4-6.
*Vulkan-Verlag: Silicone: Chemie und Technologie*: Figure 5-8.
*W. B. Saunders Company: Orthopedic Clinics of North America*: Figure 4-28 (*20*, **1989**, 1).
*Wiley/Wiley-VCH: Advanced Materials*: Figures 4-33 and 4-34 (*7*, **1995**, 609), Figure 6-17 (*5*, **1993**, 127);

*Angewandte Chemie*: Figure 2-29 (*107*, **1995**, 2515), Figures 3-30 and 3-31 (*101*, **1989**, 815), Figure 5-12 (*101*, **1989**, 1773), Figures 6-28 and 6-30 (*43*, **2004**, 2334), Figures 7-16 and 7-17 (*41*, **2002**, 1853);
D. M. Adams, *Inorganic Solids:* Figure 2-22;
D. W. Bruce, D. O'Hare (Eds.), *Inorganic Materials*: Figure 4-24 and 4-25;
*Chemie in unserer Zeit*: Figure 4-20 and Figure 4-22 (*33*, **1999**, 6), Figure 6-22 (*42*, **1995**, 1);
*Encyclopedia of Chemical Technology*, Kirk-Othmer: Figure 4-40;
R. K. Iler, *The Chemistry of Silica*: Figure 4-51;
L. V. Interrante, M. Hampden-Smith (Eds.), *Chemistry of Advanced Materials – an Overview*: Figures 3-14 and 3-21, Table 4-2;
K. J. Klabunde (Ed.), *Nanoscale Materials in Chemistry*: Figures 7-5 and 7-12;
Kittel, *Introduction to Solid State Physics*: Figure 7-11.
T. Kodas, M. Hampden-Smith (Eds.), *The Chemistry of Metal CVD*: Figures 3-16 and 3-18;
S. Mann (Ed), *Biomimetic Materials Chemistry*: Figure 4-25, Figure 4-26, Figure 4-27 and 4-32;
*Nachrichten aus Chemie, Technik und Laboratorium*: Figure 4-30 (*47*, **1999**, 1405);
*Ullmann's Encyclopedia of Technical Chemistry*: Figure 4-41;
M. T. Weller, *Anorganische Materialien*: Figure 2-2;
J. Zarzycki (Ed.), *Materials Science and Technology*: Figures 4-7 and 4-10;
*Zeitschrift für Anorganische und Allgemeine Chemie*: Figure 2-21 (*277*, **1954**, 156).

The following figures were taken from internet pages:

Figure 2-3: www.spectraweb.ch/~hwiehl/supra.html
Figure 2-8: www.ifm.liu.se/Matephys/new_page/research/sic/Chapter3.html
Figure 2-12: www.benchmarkceramics.com/Technologies/CCS/techinfo.html
Figure 2-13: www.railway-technology.com/contractors/track/elektro/elektro1.html
Figure 4-19: www.physics.ucsb.edu/~bettye/research/biomin/biomin.html
Figure 4-23: www.soton.ac.uk/~serg/biotech/mtb-main.htm
Figure 4-31: mmg.sechrest.com/mmg/thr/index.html
Figure 4-35b: webmineral.com/data/quartz.shtml
Figure 4-36: www.tewna.com/crystal/mcf/e_filter01.html and www.vanlong.com/Prodindex/osc/oscmain.html
Figure 4-53: www.metu.edu.tr/home/www70/who/ctas/lab/cordi.htm
Figure 6-5: indigo4.gi.rwth-aachen.de/flyer/feinguss/omg_e.htm
Figure 6-16: stardust.jpl.nasa.gov/spacecraft/capsule.html

Figure 6-18:
ruby.chemie.uni-freiburg.de/Vorlesung/Gif_bilder/Silicate/zsm5_a.gif
Figure 7-14:
www.phys.ttu.edu/~tlmde/thesis/CARBON_NANOTUBES.html

## Abbreviations

| | |
|---|---|
| AACVD | aerosol-assisted chemical vapor deposition |
| a.c. | alternating current |
| Ac | acetyl |
| acac | acetylacetonate = 2,4-pentanedionate |
| AFM | atomic force microscope (atomic force microscopy) |
| AIBN | azobis(isobutyronitrile) |
| ALD | atomic layer deposition |
| ALE | atomic layer epitaxy |
| AO | atomic orbital |
| aq | aqueous |
| Ar | aryl |
| a.u. | arbitrary units |
| BBU | basic building unit |
| b.p. | boiling point |
| Bu | butyl |
| C | critical point |
| cat | catalyst |
| CBE | chemical beam epitaxy |
| CBU | composite building unit |
| CD | compact disc |
| CDJP | controlled double jet precipitation |
| cmc | critical micelle concentration |
| CMC | ceramic matrix composite |
| CMR | colossal magnetoresistance |
| COD | cyclooctadiene |
| Cp | cyclopentadienyl |
| CTAB | cetyltrimethylammonium bromide |
| CVD | chemical vapor deposition |
| CVI | chemical vapor infiltration |
| D | dimensional |
| d.c. | direct current |
| DMF | dimethylformamide |
| DMSO | dimethylsulfoxide |
| DRAM | dynamic random access memory |
| diglyme | ethyleneglycol dimethylether |
| diphos | 1,2-bis(diphenylphosphino)ethane |
| dpm | dipivaloylmethanate (= thd or tmhd) |
| dppp | 1,3-bis(diphenylphosphino)propane |
| EDTA | (ethylenedinitrilo)tetraacetic acid |
| $E_F$ | Fermi energy (Fermi level) |

| | |
|---|---|
| Eq | equation |
| Et | ethyl |
| fcc | face centered cubic |
| G | free energy |
| g | gaseous |
| GMR | giant magnetoresistance |
| HA | hydroxylapatite |
| Hex | hexyl |
| hdp | hexagonal dense packing |
| hfac | 1,1,1,5,5,5-hexafluoroacetylacetonate (= 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) |
| HIP | hot isostatic pressing |
| HOMO | highest occupied molecular orbital |
| HTV | high-temperature vulcanizing |
| IEP | isoelectric point |
| IR | infrared |
| $k_B$ | Boltzmann constant |
| L | ligand; or Lewis base |
| l | liquid |
| LB | Langmuir–Blodgett (technique) |
| LC | liquid crystal; or liquid crystalline |
| LCVD | laser-assisted or laser-induced CVD |
| LED | light-emitting diode |
| Ln | lanthanoid |
| LPCVD | low-pressure CVD |
| LPS | liquid phase sintering |
| LR | liquid rubber |
| LUMO | lowest unoccupied molecular orbital |
| M | molar; or metal |
| MBE | molecular beam epitaxy |
| MCM | Mobil composition of matter |
| Me | methyl |
| MLE | molecular layer epitaxy |
| MMC | metal matrix composite |
| MWNT | multi-walled nanotube |
| MO | molecular orbital |
| MO... | metal organic ... |
| MOF | metal–organic framework |
| NLO | non-linear optic |
| OAc | acetate |
| OM... | organometallic ... |
| p | para; or pressure |
| $p_c$ | critical pressure |

| | |
|---|---|
| PACVD | plasma-assisted CVD |
| PE | polyethylene |
| PECVD | plasma-enhanced CVD |
| Ph | phenyl |
| phen | phenanthroline |
| PMMA | poly(methylmethacrylate) |
| PMC | polymer matrix composite |
| POSS | polyhedral oligomeric silsesquioxane |
| Pr | propyl |
| PTFE | poly(ethyleneterephthalate) |
| PZC | point of zero charge |
| PZT | lead zirconate titanate |
| PVD | physical vapor deposition |
| py | pyridine |
| R | organic group |
| RAM | random access memory |
| r.f. | radio frequency |
| RHEED | reflection high-energy electron diffraction |
| ROP | ring-opening polymerization |
| RPCVD | remote-plasma chemical vapor deposition |
| RTV | room-temperature vulcanizing |
| s | solid |
| SAM | self-assembled monolayer |
| SAW | surface acoustic wave |
| SBU | secondary building unit |
| SCF | supercritical fluid |
| sec | secondary |
| SET | single-electron transfer |
| SHS | self-propagating high-temperature synthesis |
| SIMIT | size-induced metal-insulator transition |
| SSM | solid-state metathesis |
| STM | scanning tunneling microscope |
| SWNT | single-walled nanotube |
| $t_{gel}$ | gel time |
| $T_{ad}$ | adiabatic temperature |
| $T_c$ | critical temperature, or Curie temperature |
| $T_g$ | glass transition (glass transformation) temperature |
| $T_m$ | melting temperature |
| TBA | *tert.* butylarsine |
| TEM | transmission electron microscopy |
| TEOS | tetraethoxysilane (tetraethylorthosilicate) |
| TOPO | trioctylphosphineoxide |
| tert | tertiary |

| | |
|---|---|
| thd | tetramethylheptanedionate (= tmhd or dpm) |
| THF | tetrahydrofuran |
| tmhd | tetramethylheptanedionate (= thd or dpm) |
| TMOS | tetramethoxysilane (tetramethylorthosilicate) |
| Tr | triple point |
| TTT curve | time–temperature-transformation curve |
| UHV | ultra-high vacuum |
| UV | ultraviolet |
| Vi | vinyl |
| VPE | vapor phase epitaxy |
| VTMS | vinyltrimethylsilane |
| wt | weight |
| XRD | X-ray diffraction |
| YBCO | yttrium barium copper oxide (high-temperature superconductor) |

# Table of Contents