

Cambridge University Press

978-0-521-42418-9 - Chemical Synthesis of Advanced Ceramic Materials

David Segal

Frontmatter

[More information](#)

Chemistry of Solid State Materials

Chemical synthesis of advanced ceramic materials

Cambridge University Press

978-0-521-42418-9 - Chemical Synthesis of Advanced Ceramic Materials

David Segal

Frontmatter

[More information](#)

Chemistry of Solid State Materials

Series Editors

A. R. West, Reader in Chemistry, University of Aberdeen

H. Baxter, formerly at the Laboratory of the Government Chemist,
London

Cambridge University Press

978-0-521-42418-9 - Chemical Synthesis of Advanced Ceramic Materials

David Segal

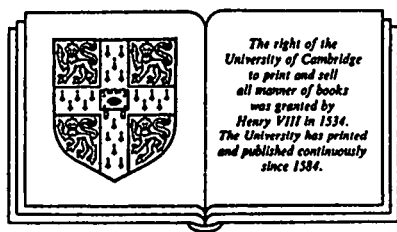
Frontmatter

[More information](#)

Chemical synthesis of advanced ceramic materials

David Segal

Materials Chemistry Department, Harwell Laboratory, Oxfordshire



Cambridge University Press

Cambridge

New York Port Chester Melbourne Sydney

Cambridge University Press
978-0-521-42418-9 - Chemical Synthesis of Advanced Ceramic Materials
David Segal
Frontmatter
[More information](#)

Published by the Press Syndicate of the University of Cambridge
The Pitt Building, Trumpington Street, Cambridge CB2 1RP
40 West 20th Street, New York, NY 10011-4211, USA
10 Stamford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1989

First published 1989
First paperback edition 1991

Printed in Great Britain at the University Press, Cambridge

British Library cataloguing in publication data

Segal, David
Chemical synthesis of advanced ceramic
materials
I. Materials. Ceramics. Synthesis
I. Title II. Series
620.1'4

Library of Congress cataloguing in publication data

Segal, David, 1950-
Chemical synthesis of advanced ceramic material / David Segal.
p. cm.
Bibliography: p.
Includes index.
ISBN 0 521 35436 6
I. Ceramics. I. Title.
TP815.S465 1989
666—dc 19 88-27537 CIP

ISBN 0 521 35436 6 hardback
ISBN 0 521 42418 6 paperback

**Transferred to
Digital Reprinting 1999**

**Printed in the
United States of America**

Cambridge University Press

978-0-521-42418-9 - Chemical Synthesis of Advanced Ceramic Materials

David Segal

Frontmatter

[More information](#)

Dedicated to my mother and father

Contents

Preface *xi*

Symbols *xiii*

- 1 Introduction: the variety of ceramic systems**
 - 1.1 Introduction *1*
 - 1.2 From traditional to advanced ceramics *1*
 - 1.3 Structural and refractory applications of engineering ceramics *2*
 - 1.4 Electroceramics *10*
 - 1.5 High-temperature oxide superconductors *10*

- 2 Conventional routes to ceramics**
 - 2.1 Introduction *17*
 - 2.2 Precipitation from solution *17*
 - 2.3 Powder mixing techniques *19*
 - 2.4 Fusion routes to ceramics *20*
 - 2.5 The need for improved synthetic routes to advanced ceramics *22*

- 3 Ceramic fabrication**
 - 3.1 Introduction *23*
 - 3.2 Solid-state sintering *23*
 - 3.3 Uniaxial pressing *25*
 - 3.4 Hot uniaxial pressing *26*
 - 3.5 Isostatic pressing *26*
 - 3.6 Reaction-bonding *27*
 - 3.7 Slip casting *28*
 - 3.8 Injection molding *28*
 - 3.9 Strength and toughness in ceramic systems *29*

Contents

- 4 Sol-gel processing of colloids**
 - 4.1 Introduction 33
 - 4.2 The nature of colloids 33
 - 4.3 The stability of colloids 34
 - 4.4 Sol formation through cation hydrolysis 39
 - 4.5 Outline of the sol-gel process for colloids 40
 - 4.6 Sol-gel in the nuclear industry 42
 - 4.7 Gel precipitation in the nuclear industry 44
 - 4.8 Industrial applications of sol-gel processing 44
 - 4.9 Summary 56

- 5 Sol-gel processing of metal-organic compounds**
 - 5.1 Introduction 58
 - 5.2 The synthesis of metal alkoxides 58
 - 5.3 The physical properties of alkoxides 60
 - 5.4 Outline of the sol-gel process for alkoxides 62
 - 5.5 Development of the sol-gel process for alkoxides 63
 - 5.6 Alkoxide-derived coatings 75
 - 5.7 Monodispersed sub-micrometre oxide powders 82
 - 5.8 Organically modified silicates 87
 - 5.9 Summary 88

- 6 Non-aqueous liquid-phase reactions**
 - 6.1 Introduction 89
 - 6.2 The reaction between silicon tetrachloride and ammonia in the liquid phase 89
 - 6.3 General reactions of chlorosilanes with ammonia and amines 95
 - 6.4 Synthesis of non-oxide ceramics other than silicon nitride using liquid-phase reactions 96
 - 6.5 Summary 98

- 7 Polymer Pyrolysis**
 - 7.1 Introduction 99
 - 7.2 Synthesis of polysilanes 99
 - 7.3 The polysilane-polycarbosilane conversion 101
 - 7.4 β -Silicon carbide fibres from polycarbosilanes 103
 - 7.5 Polysilastyrene 107
 - 7.6 Nitride and oxynitride fibres by polymer pyrolysis 108
 - 7.7 Composites, monoliths and coatings derived from polymer pyrolysis 111
 - 7.8 Summary 113

Contents

- 8 Hydrothermal synthesis of ceramic powders**
- 8.1 Introduction 114
- 8.2 Forced hydrolysis of solutions at elevated temperatures and pressures 114
- 8.3 Hydrothermal reactions using salt solutions 115
- 8.4 Hydrothermal reactions involving phase transformations 120
- 8.5 Hydrothermal reactions using metal reactants 123
- 8.6 Summary 123
- 9 Gas-phase reactions**
- 9.1 Introduction 124
- 9.2 Gas-phase nucleation 124
- 9.3 Flame-hydrolysed powders 127
- 9.4 Direct nitridation and carbothermic reduction 128
- 9.5 Non-plasma gas-phase reactions 131
- 9.6 Plasma reactions 136
- 9.7 The silicon–sulphur–nitrogen system 139
- 9.8 Electron-beam evaporation 141
- 9.9 Summary 142
- 10 Miscellaneous synthetic routes to ceramic materials**
- 10.1 Introduction 143
- 10.2 The citrate gel process 143
- 10.3 Pyrolysis of metal alkoxides 144
- 10.4 Rapid expansion of supercritical solutions 145
- 10.5 Freeze-drying 146
- Appendix Determination of particle size**
- A.1 Introduction 148
- A.2 Gas adsorption 148
- A.3 X-ray line broadening 150
- A.4 Transmission electron microscopy 150
- A.5 Scanning electron microscopy 150
- A.6 Light scattering 151
- A.7 Small-angle X-ray and neutron scattering 153
- A.8 Sedimentation methods 154
- A.9 Chromatographic methods 155
- A.10 Sieving 155
- References 156**
- Index 180**

Preface

Advanced ceramic materials have attracted increasing attention throughout the 1980s from many disciplines including chemistry, physics, metallurgy and materials science and this multidisciplinary approach is illustrated by the diverse range of journals and conferences where information is disseminated. In addition the discovery of high-temperature ceramic superconductors in 1986 has raised the profile of advanced ceramics activities not only within the scientific community but also among the general public. Attendance at conferences and surveys of scientific literature show that chemical synthetic methods have played an increasing role, over the past fifteen years, in improving the properties of ceramic materials. Books concerned with fabrication and physical properties of ceramics do not, in my opinion, highlight chemical aspects of ceramic preparations which are not the principal interest of physical, organic and inorganic chemistry textbooks.

My discussions with undergraduate and postgraduate students in chemistry and materials science as well as university lecturers and those in industry concerned with research into and manufacture of advanced ceramics produced two conclusions. Firstly, there did not seem to be a short volume available which acted as a bridge between pure chemistry and conventional ceramic studies such as fabrication. Also, although scientific publications and conference proceedings proliferate it was not obvious how a comprehensive view of the rapid inroads chemistry is making into ceramic synthesis could be obtained. I see this book as that bridge between pure chemical and conventional ceramic studies. I have included a chapter on fabrication for continuity but this is not the main theme. I have not discussed the mechanisms and structures of all reactions and materials described here, or listed 'recipes' for ceramic

Cambridge University Press

978-0-521-42418-9 - Chemical Synthesis of Advanced Ceramic Materials

David Segal

Frontmatter

[More information](#)*Preface*

synthesis. What I have attempted to show is the role chemistry has in the synthesis of advanced ceramic materials but, at all times, synthetic routes are related to the desired ceramic properties for materials in the form of powders, fibre, coatings or monoliths made on the laboratory and industrial scale. All branches of chemistry contribute to advanced ceramic development but three areas occur repeatedly throughout this book, namely colloid chemistry, homogeneous nucleation processes and chemistry at the organic–inorganic interface.

Finally, a paragraph on acknowledgements. I thank authors and copyright owners in Europe, Japan, Australia and The United States of America for giving permission to reproduce their photographs in this book. I am indebted to staff of the Harwell Library who obtained numerous scientific publications for me while line diagrams were drawn in the Tracing Office at Harwell. Anita Harvey typed the manuscript; and lastly an acknowledgement to my employer, The United Kingdom Atomic Energy Authority for permission to publish this book.

Harwell Laboratory

David Segal

Symbols

N	Avogadro number
h	Planck's constant
k	Boltzmann constant
e	Electronic charge
c	Ionic strength
z	Ion valency
%	Percentage
T	Absolute temperature
T_c	Superconducting transition or critical temperature
E	Young's modulus
S	Tensile fracture strength
$2C$	Crack length
C_1	BET constant
S_A	Surface area
D	Diffusion coefficient
D_c	Crystallite dimension
K	Equilibrium constant
K_{IC}	Fracture toughness
K^*	Constant in Scherrer equation (A.3)
G	Gravitational constant
η	Liquid viscosity
κ	Reciprocal double layer thickness
Q	Scattering vector
Ω	Angular rotational velocity
R, R'	Alkyl chain
R^*	Reflectivity at near normal incidence
R_G	Gas constant
λ	Wavelength
L	Nucleation rate per unit volume
I, I_0	Scattered intensity
$P(\phi)$	Shape factor
ϕ	Angle between incident and scattered radiation
V_L	London energy between two atoms
V_A	van der Waals – London energy for macroscopic bodies
V_R	Electrostatic energy of repulsion
V_S	Free energy due to adsorbed layer overlap
V_T	Total potential energy between particles
θ_B	Bragg angle

Symbols

$\theta_{1/2}$	Pure diffraction broadening at half-peak height
θ	Contact angle at solid-air-liquid interface
I_R	Rayleigh scattered intensity
I_{RO}	Rayleigh-Gans scattered intensity
ψ_0	Surface charge
ν_0	Ground-state electron vibrational frequency
α	Static atomic polarizability
λ^*	$= 3h\nu_0\alpha^2/4$
$A, A_1,$ A_2, A_{12}	Hamaker constant
a	Sphere radius
H_0	Separation of spheres or flat plates at closest approach
x	$= H_0/2a$
q	Number of molecules per unit volume of material
ϵ_0	Permittivity of vacuum
ϵ	Relative permittivity of medium
l	Side length of a cube
l_0	Sample to detector distance
l_1	Sedimentation distance
l_2	Distance between particle and axis of rotation
l_3	Radius of rotation for particles
$n_0, n_1, n_2,$ n_p, n_m	Refractive index
n	Number of molecules in critical cluster
$\Delta G'_n$	Free energy of formation for critical cluster
r	Distance between atoms
r_p	Pore radius
r_d	Radius of liquid droplet
r_g	Radius of gyration
r_n	Critical radius of cluster
b, f, g, j, δ	Number of moles
$t_{1/2}$	Half-life
$t, t_1, t_2,$ t_3, t_c, τ	Time
ρ, ρ_p, ρ_l	Density
γ	Surface tension of liquid
γ'	Surface energy
Δ_p	Capillary pressure
$p_F, p_G,$ p_j	Partial gas pressures
p^0	Saturation vapour pressure
p'	Vapour pressure
p	Gas pressure
M_w	Molecular weight
\bar{M}_w	Weight average molecular weight
\bar{M}_n	Number average molecular weight
h_c	Coating thickness
C_x, C_0	Concentration of solute or reactant
C_x	Saturated solute concentration

Cambridge University Press

978-0-521-42418-9 - Chemical Synthesis of Advanced Ceramic Materials

David Segal

Frontmatter

[More information](#)***Symbols***

C_{ss}	Supersaturated solute concentration
N_p	Number of particles
β	Overall growth coefficient for droplets
v	Molar volume of liquid phase
v_l	Volume of molecule in liquid phase
v_a	Adsorbate volume at a specified relative pressure
v_m	Adsorbate volume for monolayer coverage per unit mass of solid
m	Mass of a molecule
m_d	Volume of a diffusing vacancy
M	Metal