



S C I E N C E O F  

---

**CERAMIC CHEMICAL  
PROCESSING**

EDITED BY

**LARRY L. HENCH**

*University of Florida  
Gainesville, Florida*

**DONALD R. ULRICH**

*Air Force Office of Scientific Research  
Washington, D.C.*

A WILEY-INTERSCIENCE PUBLICATION

**JOHN WILEY & SONS**

New York

Chichester

Brisbane

Toronto

Singapore



Copyright©1986 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

***Library of Congress Cataloging in Publication Data***

Main entry under title:

Science of ceramic chemical processing.

“A Wiley-Interscience publication.”

Proceedings of the Second International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites, held February 25–March 1, 1985 in Palm Coast, Florida . . . sponsored by the Department of Materials Science and College of Engineering, University of Florida”—Pref.

Includes index.

1. Ceramics—Congresses. 2. Glass—Congresses. 3. Composite materials—Congresses. 4. Colloids—Congresses. I. Hench, L. L. II. Ulrich, Donald R. III. University of Florida. Department of Materials Science and Engineering. IV. University of Florida. College of Engineering. V. International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites (2nd: 1985: Palm Coast, Fla.)

TP785.S35 1986  
ISBN 0-471-82645-6

666

85-22490

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

S C I E N C E O F

---

**CERAMIC CHEMICAL  
PROCESSING**



Front row left to right: Dr. Ralph Iler, Keynote Awardee for inorganic chemistry; Prof. Paul Flory, Keynote Awardee for organic and polymer chemistry; Prof. Per-Olov Löwdin, Keynote Awardee for quantum chemistry. Second row left to right are presenters of Keynote Awards: Dr. George Parshall, Director of Chemistry Research, E. I. duPont de Nemours presenter of Dr. Iler's Keynote Award; Mr. Marshall Criser, President of the University of Florida, presenter of Prof. Löwdin's Keynote Award; Dr. Leo Young, Director, Research and Laboratory Management, Office of the Under Secretary of Defense, presenter of Prof. Flory's Keynote Award.

## CONTRIBUTORS

W. WADE ADAMS  
AFML  
Department of the Air Force  
Wright-Patterson AFB, Ohio

ILHAN A. AKSAY  
Department of Materials Science  
and Engineering  
University of Washington  
Seattle, Washington

I. ARTAKI  
Department of Chemistry  
School of Chemical Sciences  
University of Illinois  
Urbana, Illinois

JAMES H. AUBERT  
Sandia National Laboratories  
Albuquerque, New Mexico

P. H. BARBOUX  
Spectrochimie due Solide,  
Université Paris  
Paris, France

E. A. BARRINGER  
Ceramics Process System  
Corporation  
Lexington, Massachusetts

KRIS A. BERGLUND  
Departments of Agricultural and  
Chemical Engineering  
Michigan State University  
East Lansing, Michigan

ELIZABETH K. BONDERSON  
Department of Chemistry  
North Dakota State University  
Fargo, North Dakota

PHILIP BOUDJOUK  
Department of Chemistry  
North Dakota State University  
Fargo, North Dakota

H. K. BOWEN  
Ceramic Processing Research  
Laboratory  
Materials Processing Center  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

M. BRADLEY  
Department of Chemistry  
School of Chemical Sciences  
University of Illinois  
Urbana, Illinois



C. J. BRINKER  
Sandia National Laboratories  
Albuquerque, New Mexico

H. A. BUMP  
Rockwell International  
Thousand Oaks, California

Larry W. Burggraf  
Department of Chemistry  
Air Force Academy  
Colorado Springs, Colorado

LEE A. CARMAN  
Department of Materials Science  
and Engineering  
Pennsylvania State University  
University Park, Pennsylvania

YEU-CHYI CHENG  
Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

D. E. CLARK  
Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

M. J. CRIMP  
Department of Metallurgy and  
Materials Science  
Case Western Reserve University  
Cleveland, Ohio

LARRY P. DAVIS  
Department of Chemistry  
Air Force Academy  
Colorado Springs, Colorado

I. DJUROVICH  
Department of Chemistry  
University of Wisconsin  
Madison, Wisconsin

R. G. DOSCH  
Sandia National Laboratories  
Albuquerque, New Mexico

W. F. DOYLE  
Department of Metallurgy and  
Materials Science  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

B. D. FABES  
Department of Metallurgy and  
Materials Science  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

D. L. FEKE  
Department of Chemical  
Engineering  
Case Western Reserve University  
Cleveland, Ohio

Paul J. Flory  
Department of Chemistry  
Stanford University  
Stanford, California

SETH FRADEN  
Martin Fisher School of Physics  
Brandeis University  
Waltham, Massachusetts

K. J. FRANKLIN  
Atomic Energy of Canada Ltd.  
Chalk River Laboratories  
Chalk River, Ontario, Canada

K. G. FRASE  
National Bureau of Standards  
Gaithersburg, Maryland

DAVID R. GAGNON  
Department of Polymer Science  
and Engineering  
University of Massachusetts  
Amherst, Massachusetts

MARK S. GORDON  
Department of Chemistry  
North Dakota State University  
Fargo, North Dakota

THIERRY GRANIER  
Department of Polymer Science  
and Engineering  
University of Massachusetts  
Amherst, Massachusetts

J. W. HALLORAN  
Department of Metallurgy and  
Materials Science  
Case Western Reserve University  
Cleveland, Ohio

R. H. HEISTAND II  
Dow Chemical USA  
New England Laboratory  
Wayland, Massachusetts

THADDEUS E. HELMINIAK  
Polymer Branch  
Materials Laboratory  
Air Force Wright Aeronautical  
Labs  
Wright Patterson AFB, Ohio

LARRY L. HENCH  
Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

GEORGE K. HENRY  
Loker Hydrocarbon Research  
Institute  
Department of Chemistry  
University of Southern California  
Los Angeles, California

ARLON J. HUNT  
Applied Science Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California

ALAN J. HURD  
Department of Chemistry  
University of New Mexico  
Albuquerque, New Mexico

RALPH K. ILER  
811 Haines Avenue  
Wilmington, Delaware

N. A. IVES  
Chemistry and Physics Laboratory  
The Aerospace Corporation  
El Segundo, California

D. W. JOHNSON, JR.  
AT&T Bell Laboratories  
Murray Hill, New Jersey

R. E. JOHNSON, JR.  
E.I. DuPont de Nemours & Co.  
Central Research & Development  
Department  
Experimental Station  
Wilmington, Delaware

J. P. JOLIVET  
Chimie des Polymeres Inorganiques  
Université Pierre et Marie Curie  
Paris, France

JIRI JONAS  
Department of Chemistry  
School of Chemical Sciences  
University of Illinois  
Urbana, Illinois

Alfred Kaiser  
Fraunhofer-Institute für  
Silicatiforschung  
Wurzburg, West Germany

FRANK E. KARASZ  
Materials Research Laboratory  
University of Massachusetts  
Amherst, Massachusetts

K. D. KEEFER  
Sandia National Laboratories  
Albuquerque, New Mexico

BRUCE KELLETT  
Department of Materials Science  
and Engineering  
University of California  
Los Angeles, California



R. KIKUCHI  
Department of Materials Science  
and Engineering  
University of Washington  
Seattle, Washington

SUNUK KIM  
Institute of Glass Science  
and Engineering  
New York State College of Ceramic  
Ceramics  
Alfred University  
Alfred, New York

L. C. KLEIN  
Department of Ceramics  
Rutgers University  
The State University of  
New Jersey  
Piscataway, New Jersey

SRIDHAR KOMARNENI  
Materials Research Laboratory  
Pennsylvania State University  
University Park, Pennsylvania

G. KORDAS  
Mechanical and Materials  
Engineering  
Vanderbilt University  
Nashville, Tennessee

MASATO KUMAGAI  
Department of Materials Science  
and Engineering  
Pennsylvania State University  
University Park, Pennsylvania

WILLIAM C. LACOURSE  
Institute of Glass Science  
and Engineering  
Alfred University  
Alfred, New York

J. J. LAGOWSKI  
Department of Chemistry  
University of Texas  
Austin, Texas

F. F. LANGE  
Rockwell International Science  
Center  
Thousand Oaks, California

BURT I. LEE  
Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

AXEL LENTZ  
Abteilung für Anorganische  
Chemie  
Universität Ulm  
Ulm, West Germany

ROBERT W. LENZ  
Department of Polymer Science  
and Engineering  
University of Massachusetts  
Amherst, Massachusetts

M. S. LEUNG  
Chemistry and Physics Laboratory  
The Aerospace Corporation  
El Segundo, California

H. C. LING  
AT&T Bell Laboratories  
Murray Hill, New Jersey

R. A. Lipeles  
The Aerospace Corporation  
Los Angeles, California

J. LIVAGE  
Spectrochimie due Solide,  
Université Paris  
Paris, France

PER-OLOV LÖWDIN  
Department of Chemistry  
University of Florida  
Gainesville, Florida

KEVIN D. LOFFTUS

Applied Science Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California

J. B. MACCHESNEY

AT&T Bell Laboratories  
Murray Hill, New Jersey

J. D. MACKENZIE

Department of Materials Science  
and Engineering  
University of California  
Los Angeles, California

J. E. MARK

Department of Chemistry  
University of Cincinnati  
Cincinnati, Ohio

EGON MATIJEVIĆ

Department of Chemistry  
Clarkson University  
Postdam, New York

JAMES L. MCARDLE

Department of Materials Science  
and Engineering  
Pennsylvania State University  
University Park, Pennsylvania

GARY L. MESSING

Department of Materials Science  
and Engineering  
Pennsylvania State University  
University Park, Pennsylvania

ROBERT B. MEYER

Martin Fisher School of Physics  
Brandeis University  
Waltham, Massachusetts

W. C. MOFFATT

Ceramic Processing Research  
Laboratory  
Materials Processing Center  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

P. E. D. MORGAN

Rockwell International  
Thousand Oaks, California

BRIJ M. MOUDGIL

Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

B. NOVICH

Ceramic Processing Research  
Laboratory  
Materials Processing Center  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

Y. OGURI

Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

H. OKAMURA

Nippon Soda Company  
New York, New York

GEORGE Y. ONODA

IBM  
Thomas J. Watson Research Center  
Yorktown Heights, New York

GERARD ORCEL

Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

CARLO G. PANTANO

Materials Science and Engineering  
Pennsylvania State University  
University Park, Pennsylvania

S. C. PARK

Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

I. PETER

Department of Chemistry  
University of Wisconsin  
Madison, Wisconsin

T. M. PETTIJOHN

Department of Chemistry  
University of Texas  
Austin, Texas

J. PHALIPPOU

CNRS Glass Laboratory and  
Materials Science Laboratory  
Montpellier, France

PARAS N. PRASAD

Department of Chemistry  
State University of New York  
at Buffalo  
Buffalo, New York

M. PRASSAS

Corning Europe Inc.  
Centre Europeen de Recherche  
Avon, France

E. A. PUGAR

Rockwell International  
Thousand Oaks, California

E. M. RABINOVICH

AT&T Bell Laboratories  
Murray Hill, New Jersey

PETER B. RAND

Sandia National Laboratories  
Albuquerque, New Mexico

J. J. RATTO

Rockwell International  
Thousand Oaks, California

W. W. RHODES

AT&T Bell Laboratories  
Murray Hill, New Jersey

J. J. RITTER

National Bureau of Standards  
Gaithersburg, Maryland

E. P. ROTH

Sandia National Laboratories  
Albuquerque, New Mexico

RUSTUM ROY

Materials Research Laboratory  
Pennsylvania State University  
University Park, Pennsylvania

MICHAEL RUDOLPH

Abteilung für Anorganische Chemie  
Universität Ulm  
Ulm, West Germany

MICHAEL D. SACKS

Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

DALE W. SCHAEFER

Sandia National Laboratories  
Albuquerque, New Mexico

G. W. SCHERER

Corning Glass Works  
R&D Division  
Corning, New York

HELMUT SCHMIDT

Fraunhofer-Institut für  
Silicatforschung  
Würzburg, West Germany

DIETMAR SEYFERTH

Department of Chemistry  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

RICHARD A. SHELEMAN

Department of Materials Science  
and Engineering  
Pennsylvania State University  
University Park, Pennsylvania



RONG-SHENG SHEU  
Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

L. SILVERMAN  
Department of Materials Science  
and Engineering  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

YOSHIKO SOWA  
Materials Research Laboratory  
Pennsylvania State University  
University Park, Pennsylvania

R. F. STEWART  
ICI Corporate Colloid Science  
Group  
The Heath Runcorn  
Cheshire, England

HAROLD STÜGER  
Department of Chemistry  
University of Wisconsin  
Madison, Wisconsin

D. SUTTON  
ICI PLC  
Corporate Colloid Science Center  
The Heath Runcorn  
Cheshire, England

D. R. TALLANT  
Sandia National Laboratories  
Albuquerque, New Mexico

PARAM H. TEWARI  
Applied Science Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California

E. TRONC  
Spectrochimie due Solide,  
Université Paris  
Paris, France

THANH N. TRUNOG  
Department of Chemistry  
North Dakota State University  
Fargo, North Dakota

C. W. TURNER  
Atomic Energy of Canada Limited  
Chalk River Nuclear Laboratories  
Chalk River, Ontario,  
Canada

D. R. UHLMANN  
Department of Metallurgy and  
Materials Science  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

DONALD R. ULRICH  
Department of the Air Force  
Air Force Office of Scientific  
Research  
Bolling AFB, Washington, D.C.

S. Wallace  
Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

S. H. WANG  
Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

S. B. WARNER  
Kimberly-Clark  
Roswell, Georgia

WILLIAM P. WEBER  
Department of Chemistry  
University of Southern California  
Los Angeles, California

ROBERT WEST  
Department of Chemistry  
University of Wisconsin  
Madison, Wisconsin

GARY H. WISEMAN  
Department of Chemistry  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

K. W. WISTROM  
Department of Materials Science  
and Engineering  
University of Florida  
Gainesville, Florida

M. F. YAN  
AT&T Bell Laboratories  
Murray Hill, New Jersey

J. ZARZYCKI  
Materials Science Laboratory  
University of Montpellier  
Montpellier, France

B. J. ZELINSKI  
Department of Materials Science  
and Engineering  
Massachusetts Institute of  
Technology  
Cambridge, Massachusetts

T. W. ZERDA  
Department of Chemistry  
School of Chemical Sciences  
University of Illinois  
Urbana, Illinois

XING-HUA ZHANG  
Department of Chemistry  
University of Wisconsin  
Madison, Wisconsin

*In Memoriam*

PAUL J. FLORY  
Nobel Laureate  
June 19, 1910–Sept. 8, 1985

RALPH K. ILER  
July 12, 1909–November 9, 1985

## PREFACE

This book contains the proceedings of the "Second International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites, held February 25–March 1, 1985 in Palm Coast, Florida. The conference was sponsored by the Department of Materials Science and College of Engineering, University of Florida and supported by the Directorate of Chemical and Atmospheric Sciences of the Air Force Office of Scientific Research. More than 250 scientists and engineers from university, industry, and government laboratories attended the conference, including researchers from the United States, Canada, England, France, Italy, Japan, and West Germany.

Three Keynote Award lectures were presented. Dr. Ralph Iler's Keynote Award was given for a lifetime's contribution to inorganic chemistry. His pioneering work in the study of silica polymerization and colloidal chemistry is the foundation of many of the concepts explored in Parts 1, 2, and 5 of this book.

Professor Paul Flory's Keynote Award was given for a lifetime's contribution to polymer chemistry. His developments in the theory of organic networks and structures provide the basis for interpreting many of the new materials developments discussed in Parts 1, 3, and 4 of this book.

Professor Per-Olov Löwdin's Keynote Award was given for a lifetime's contribution to quantum chemistry. His organization and chairmanship of the Sanibel Conference for 25 years have been a major influence on quantum calculations being directed toward practical applications such as the silicon-based systems discussed in Parts 3 and 4.

The concept of chemically based ultrastructure processing involves a synthesis of the fields of inorganic chemistry, organic chemistry, polymer chemistry, surface chemistry, and quantum chemistry, all oriented toward producing a new generation of high-performance materials. The three keynote awardees have provided much of the foundation for that synthesis.



In addition to the three keynote lectures, 34 of 36 oral presentations and 23 of 42 poster papers are included, selected after peer review by the conference review board. The resulting 60 chapters were organized into six parts: sol-gel science, applications of sol-gel processing, materials from organometallic precursors, ultrastructure in macromolecular materials, micromorphology (fine particulate) science, and quantum chemistry (a review).

Consequently, this book provides a comprehensive treatment of the broad scientific basis of producing ceramic, glass, and composite materials using chemistry-based processing methods.

It is the goal of ultrastructure processing to control the structure, surfaces, and interfaces of materials and devices at the molecular level in the earliest stages of production. The scientific understanding of molecular structure control of complex materials is beginning to emerge, as is evident in this volume. However, there is still much to be learned that will require multiple investigator efforts. The beginnings of such interdisciplinary efforts are evident herein. The long-term consequences of this new approach to creating complex materials from a molecular viewpoint are just beginning to emerge. The potential rewards are enormous.

LARRY L. HENCH  
DONALD R. ULRICH

*Gainesville, Florida*  
*Washington, D.C.*  
*January 1986*

S C I E N C E O F

---

**CERAMIC CHEMICAL  
PROCESSING**

# CONTENTS

## PART 1 SOL–GEL SCIENCE

- |           |                                                                                                      |           |
|-----------|------------------------------------------------------------------------------------------------------|-----------|
| <b>1</b>  | <b>Inorganic Colloids for Forming Ultrastructures</b>                                                | <b>3</b>  |
|           | <i>Ralph K. Iler</i>                                                                                 |           |
| <b>2</b>  | <b>Physical-Chemical Factors in Sol–Gel Processes</b>                                                | <b>21</b> |
|           | <i>J. Zarzycki</i>                                                                                   |           |
| <b>3</b>  | <b>Relationships Between Sol to Gel to Glass Conversions: Structure of Gels During Densification</b> | <b>37</b> |
|           | <i>C. J. Brinker, E. P. Roth, D. R. Tallant, and G. W. Scherer</i>                                   |           |
| <b>4.</b> | <b>Use of Drying Control Chemical Additives (DCCAs) in Controlling Sol–Gel Processing</b>            | <b>52</b> |
|           | <i>Larry L. Hench</i>                                                                                |           |
| <b>5</b>  | <b>Kinetics and Mechanisms of Sol–Gel Polymerization</b>                                             | <b>65</b> |
|           | <i>Jiri Jonas</i>                                                                                    |           |
| <b>6</b>  | <b>NMR, Raman Study of the Effect of Formamide on the Sol–Gel Process</b>                            | <b>73</b> |
|           | <i>I. Artaki, M. Bradley, T. W. Zerda, Jiri Jonas, G. Orcel, and Larry L. Hench</i>                  |           |