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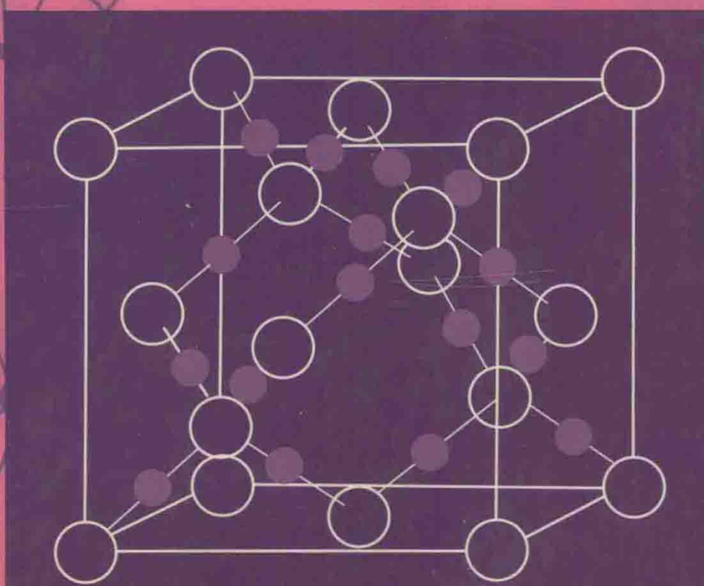
THE CHEMISTRY OF CERAMICS



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THE CHEMISTRY OF CERAMICS

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THE CHEMISTRY OF CERAMICS

PREFACE TO THE ENGLISH VERSION

Since 'The Chemistry of Ceramics' was first published by Maruzen in 1982, I am delighted to say that it has been adopted as a textbook for courses at many universities and technical colleges. This would seem to indicate that the authors correctly recognised a need for such a book and produced one that fulfilled lecturers needs exactly. The book is written primarily for students with a chemistry background with less descriptive detail than a traditional textbook on ceramic materials and products and a different emphasis than would be required by students of physics. The authors' intentions have been to present their perspective on ceramic materials assuming the reader has an understanding of the basic science involved.

The use of ceramics goes back many thousands of years, however until recently, the history of ceramics and knowledge gained had not been systematically documented. The first edition of this book was an important step towards this.

The advanced ceramics industry has progressed greatly since then. For example; Information Technology is now based upon a variety of materials, amongst which electric ceramics play an important role; the precision machining industry could not exist without high performance machinery ceramics and many environmental monitors are now made of ceramics, including automobile exhaust sensors. Ceramics are also proving to be very promising materials for generating clean energy.

Along with the development of the advanced ceramics industry, scientific knowledge of the materials has been accumulated and systemised. Since the first edition, I have been trying to revise the content and the first major opportunity I had to do this was when Maruzen decided to publish a second edition in 1993. This English version is primarily based on the second edition and the content has been thoroughly checked and revised where necessary during the translation process. I am proud to say that the second edition was also well received and is now thought of as *the* standard textbook for ceramics.

The science of ceramics and the ceramics industry in Japan have developed and improved greatly over the last twenty years. This book is regularly consulted by many people working in the field especially when trying to gain a clearer scientific perspective on ceramics.

I am very grateful to my publishers, Maruzen and John Wiley & Sons for giving me the opportunity to edit the English version and would also like to thank Hisao Yamada for the excellent job he has done in translating the book. It is a remarkable coincidence that I am now based in London for much of the time in my position as the first director of the Japan Society for the Promotion of Science, as well as retaining my principal job as Professor of Ceramics and intelligent materials at the University of Tokyo. I hope and believe that this English version will help the development of ceramic science and industry worldwide.

Mid-December 1995

Hiroaki Yanagida
Principal Author

PREFACE TO THE FIRST EDITION

The progress of technology has been supported by the development of new materials. Ceramics, which makes up the three major classes of materials along with metals and plastics, have made remarkable progress since the early 1970s. Progress in integrated circuits has been supported by the development of alumina substrates. Optical fibers for telecommunications have been commercialized since the establishment of manufacturing processes for high-purity glass fibers. The performance of cutting tools has been improved by the introduction of hard ceramics such as diamonds. Ceramics with superior electromagnetic, optical and chemical characteristics along with conventional ceramic characteristics such as hardness, refractoriness and anti-corrosion properties have emerged as a group of high-precision ceramics which are now called fine ceramics. It is widely anticipated that the science and technology of ceramics will develop further in the future. Ceramics will be applied widely in combustion engines, energy development, medical implants and microelectronics.

In order to understand ceramics in detail and to provide a stepping stone for further development, it is necessary to have a concise textbook which covers a wide variety of subjects from basics to applications. Ceramics textbooks in the market today are either too obsolete without any coverage of new ceramics or too voluminous due to the inclusion of a wide variety of subjects.

In order to overcome these shortcomings in existing textbooks, attempts have been made in this book to cover the minimal number of essential concepts for understanding ceramics. Thus the book employs a group of terminology for chemistry and is intended for young chemistry students. This book is based on my lectures on 'Solid State Chemistry' at Tokyo University. Fifteen lectures, each an hour and a half long, were given to undergraduate students whose major was Applied Chemistry. The lectures have now been expanded to solid structures and solid reactions and are given in 22 to 23 sessions. The manuscript has been assisted by Drs Kunihiko Koumoto (now Professor at Nagoya University) and Masaru Miyayama, two associate professors at University of Tokyo, who audited my lectures. Because of the involvement of these researchers I believe that the book has been written consistently from the viewpoint of chemistry. I would like to take this opportunity to thank both of them.

It is my pleasure to see that this book contributes in furthering the interests of ceramics, provides a basic understanding in ceramics from chemical viewpoints and becomes a stepping stone for the further development of ceramics.

Finally I would like to acknowledge the assistance of the staff at Maruzen Publishing Company for the publication of this book.

Early spring, 1982

Hiroaki Yanagida
Author/Editor

PREFACE TO THE SECOND EDITION

More than ten years have passed since the first publication of this book in the applied chemistry series. During the period ceramics have made remarkable progress both scientifically and technically. Some of the examples are as follows. Ceramic turbochargers have been commercialized as components in automobile engines. A group of ceramics has been discovered to exhibit superconductivity at high temperatures, which was unthinkable ten years ago. Also, piezoelectric motors without a coil have been introduced commercially.

This book was written originally to cover the chemistry of ceramics from basics to applications so that readers would obtain an understanding of the physical properties of ceramics. In light of the remarkable progress in ceramics over the last ten years it occurred quite naturally to the authors to revise the book by incorporating some new and interesting topics.

The authors have also gained invaluable experience during the last ten years. The editor (Yanagida) played a leading role in the establishment of the Research Center for Advanced Technologies in May 1987 at Tokyo University and was the director of the Center from April 1989 to March 1991. During the period he led educational and research activities at the Center with academic excellence, internationality, openness and mobility as his motto. He felt strongly about the needs of research as well as development activities, and he began with these ideals. One of the co-authors, Dr Kunihito Koumoto who was an associate professor ten years ago, has been appointed a professor at the Faculty of Engineering at Nagoya University, a Mecca of ceramics in Japan. Dr Masaru Miyayama, who was a senior research associate ten years ago, participated in the establishment of the Research Center for Advanced Technologies as an associate professor from its inception. He is playing a leading role at the Center today. We have made every effort to reflect our experience in revising the book. A wide acceptance of the first edition made it possible to obtain the cooperation of the Maruzen Publishing Company for a revision.

It is hoped that this book will contribute to the further development of the science and technology of ceramics.

Mid-autumn 1993

Hiroaki Yanagida,
Author/Editor

CONTENTS

1

INTRODUCTION

1.1 THE POSITION OF CERAMICS IN MATERIALS SCIENCE

Ceramics have been defined as non-metallic, inorganic solid materials produced by thermal treatment. Compared to metals and plastics, ceramics are hard, non-combustible and non-oxidizable. Thus they can be used in severe high-temperature, corrosive and tribological environments. In addition, many ceramics exhibit superior electromagnetic, optical and mechanical properties under these environments. Because of these unique characteristics, ceramics have been increasingly sought for energy development and advanced telecommunications.

The term 'material' is the most important aspect of the above definition of ceramics. Without this term, even volcanic ash and lava can be regarded as ceramics. If it is not possible to fabricate shapes with given dimensions, it is no use having a new inorganic substance with superior properties. Although the gap between a substance and a material is quite small in metals and plastics (due to their easier fabrication), the difference is significant in ceramics.

Ceramic materials which overcame this gap in the past include porcelains, glasses and cements. Porcelains are made of three essential ingredients, namely, siliceous stone as a skeletal ingredient, clay as a forming additive and feldspar as a sintering additive. These three ingredients have three essential functions, namely, plasticity of aqueous slurry from clay, dry strength, and bonding of siliceous stones by the fusion of feldspar during sintering. In order to manufacture porcelains into desired shapes and to provide functionality it is essential to have these three materials. Siliceous stone, clay and feldspar are all silicate minerals.

Glasses soften when heated and it becomes possible to fabricate them into shapes. When cooled to room temperature, glasses retain their shape at high temperatures and thus become materials. The major ingredients of glasses are soda ash and a silicate which contains some calcium oxide. When mixed with water, cements become plastic and it becomes possible to fabricate shapes. During subsequent hydration, an aqueous mixture of a cement coagulates and solidifies into a desired shape. Calcium silicates are the major ingredients of cements. Since porcelains, glasses and cements all contain silicates, the manufacture of these ceramics is classified as the silicate industry. The main functionality of these ceramics is either structural or containment.

Silicates are not the only non-metallic, inorganic solid materials obtained by thermal treatment. Non-oxides such as nitrides and carbides and composites with metals and plastics exhibit superior properties which cannot be obtained from silicates. It is vitally important to develop manufacturing processes so that the superior functions of these substances can be fully exploited. When developed, it is possible to produce ceramic materials with superior electromagnetic, optical and mechanical functions together with the more conventional characteristics of hardness, non-combustibility and anti-corrosiveness. Manufacturing technologies of these substances have improved significantly during the last few decades and many non-metallic inorganic solids have been able to be transformed into ceramics. These new classes of ceramics are now called either new or fine ceramics. Table 1.1 lists a number of new ceramics. The distinction between new and fine ceramics can be made as follows. Those non-silicate ceramics which can be exploited for a few of their unique characteristics are called new ceramics. When most of their unique characteristics can be exploited, ceramics are called fine ceramics. Table 1.2 lists new and fine ceramic applications of alumina (Al_2O_3).

The progress of conventional ceramics to fine ceramics is summarized in Table 1.3. Characteristics of fine ceramics are compared in Table 1.4 with those of stoneware, metals and plastics. As indicated in Table 1.4, brittleness is the most significant deficiency of fine ceramics. This deficiency needs to be overcome in future.

1.2 CERAMICS IN THE HISTORY OF MATERIALS

The very first tools that human beings used were stone (e.g. spades and axes) but it was not possible to make any large and complicated shapes. Later a technique was developed to make earthenware by mixing clay with water, shaping and firing. The earthenware was used as containers, but was prone to leakage. Thus stoneware and earthenware were the precursors of ceramics. Although the stoneware was hard and resistant to both heat and water, it was very difficult to shape and fabricate. On the other hand, earthenware was easy to work but it was weak and not watertight. Therefore, in order to improve both stoneware and earthenware it was necessary to improve fabrication of the stoneware and the physical properties of the earthenware.

Bronze was the first metallic material and was used extensively to produce a variety of containers and cutting tools because of its excellent ductility. But

Table 1.1 Functions and applications of fine ceramics

Functions	Substances and states	Elements	Devices
(A) *Electrical and magnetic*			
A-1: high insulation	Al_2O_3 (HP/HD SB, SX plates)	IC substrates	ICs
	AlN (HP/HD SB)	Heat spreaders	ICs
	C (HP SX)	Heat spreaders	ICs
A-2: dielectric	$BaTiO_3$ (HP/HD SB, SX)	HC capacitors	Electronic circuits
	$Bi_2O_3 \cdot SnO_2$ (HP/HD SB)	HC capacitors	Electronic circuits
A-3: piezoelectric	Pb $(Zr_zTi_{1-z})O_3$ (polarized HD SB)	Oscillators, ignitors, filters, transformers	Ultrasonic elements, electric circuits
	ZnO (oriented thin films)	Surface elastic wave delay elements	Electronic circuits
	SiO_2 (thin film SX)	Oscillators	Watches
A-4: pyroelectric	Pb $(Zr_zTi_{1-z})O_3$ (polarized HD SB)	IR detectors	
A-5: strong dielectric	$(1-x)$ Pb $(Zr_zTi_{1-z})O_3 + xLa_2O_3$ (translucent HD SB)	Image storage elements, optoelectronic deflectors	
A-6: soft magnetic	$Zn_{1-x}Mn_xFe_2O_4$ (HD SB, GB controlled)	Memory, calculators, magnetic cores, magnetic tapes	Computers, transformers, tape recorders
	γ-Fe_2O_3 (needle-shaped fine powder)		
A-7: hard magnetic	$SrO \cdot 6Fe_2O_3$ (oriented HD SB)	Magnets	CRT
	$SrO \cdot 6Fe_2O_3$ (powder/rubber composites)	Plastic magnets	Airtight shutters for refrigerators
A-8: semiconducting	$La_{1-x}Ca_xCrO_3$ (SB)	Resistance heaters, gas sensors, thermistors	HT furnaces, gas-leak detectors, temp. controllers, lightning arresters
	SnO_2 (porous SB, Pt loaded) transition metal oxides (HD SB)		
	ZnO-Bi_2O_3 (MS-controlled SB)	Varistors	Surge arresters
	$BaTiO_3$ (MS-controlled SB)	Self-controlled resistance heaters	Electronic jars, bed dryers

(continued)

Table 1.1 *(continued)*

Functions	Substances and states	Elements	Devices
A-9: ionic conduction	β-Al_2O_3 (HD SB) stabilized zirconia (HD SB)	Na-S batteries, oxygen sensors	Load leveling for power generators Blast furnace control, air/fuel controllers for automobiles
A-10: electron emission	LaB_6	Thermal cathodes for electron guns	Thermal electron devices
A-11: superconductor	$Ba_2LaCu_3O_{7-\delta}$	Josefson junctions Superconducting magnets	High-speed computers Magnetic levitation
(B) *High hardness*			
B-1: polishing, grinding, cutting	Al_2O_3, B_4C, diamond (powders) Al_2O_3, B_4C, diamond (resin bonded) Al_2O_3, B_4C, diamond (metal bonded) TiN, TiC, B_4C, Al_2O_3 (HD SB)	Polishing, grinding stones Cutting tools Cutting tools	
B-2: mechanical strength	Si_3N_4, SiC (HD SB)	Turbine blades	Automobile engines
(C) *Optical*			
C-1: fluorescence	Y_2O_3 : Eu (powders)	Fluorescence	Color televisions
C-2: translucence	Al_2O_3 (translucent SB) SnO_2 (coating layers)	HT, CR translucent bodies Visible light-transmitting semiconductors	High-pressure sodium lamps Antifog windows
C-3: optical deflection	PLZT (see A-5 above)		
C-4: optical reflection	TiN (thin film coating)	HT metallic characteristics	Solar collectors
C-5: IR reflection	SnO_2 (thick film coating)	Visible light transmission with IR reflection	Energy-saving window panes
C-6: optical transmission	SiO_2 (HP fibers)	Optical fibers	Optical transmission cables, optical fiber cameras

(D) *Thermal*			
D-1: thermal stability	ThO_2 (HD SB)	Thermally insulating structural components	HT furnaces
D-2: thermal insulation	$K_2O{\cdot}nTiO_2$ (fibers)	Thermally stable insulators	Energy-saving furnaces
	$CaO{\cdot}nSiO_2$ (foams)	Lightweight insulators	Non-combustible insulators
D-3: thermal conduction (see A-1 above)	AlN (HP, HD SB)	Electronic substrates	ICs
	C (HP SX)	Electronic substrates	ICs
(E) *Chemical and biochemical*			
E-1: artificial bones	Al_2O_3, Ca_5 (F, Cl) P_3O_{12} (HP SB)	Artificial bones and teeth	Bioceramics
E-2: substrates	SiO_2 (porous bodies with controlled pore sizes)	Substrates for enzymes	Biochemical applications
	Al_2O_3, TiO_2 (porous bodies)	Substrates for catalysts	Chemical reaction control
E-3: catalytic	$K_2O{\cdot}nAl_2O_3$ (porous SB)	Catalysts for aqueous gas reactions	Catalytic applications at HT

CR: corrosion resistant.
HC: high capacity.
HP: high purity.
IC: integrated circuit.
MS: microstructure.
SX: single crystal.
CRT: cathode ray tube.
HD: high density.
HT: high temperature.
GB: grain boundary.
SB: sintered body.