PRINCIPLES OF ELECTRONIC CERAMICS

L. L. HENCH

J. K. WEST

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L. L. HENCH
Advanced Materials Research Center
University of Florida
Gainesville, Florida

and

J. K. WEST
Advanced Materials Research Center
University of Florida
Gainesville, Florida

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To June and Donna

For their patience, understanding, and support without which this book would still be a set of unedited, coffee-stained notes

PREFACE

Many thousands of years ago, the conversion of molded, naturally occurring clay into fired, insoluble ceramic pottery began mankind's technical mastery over nature. During the following millennia (see Figure 1), an ever-increasing ability to manipulate and control the properties of ceramic materials was achieved. These developments led to the refractories essential for production of high-melting metallic alloys. The transition from the Ages of Pottery to Bronze to Iron and Steel has culminated in our modern worldwide industrial society. Figure 1 also illustrates that the information content in these progressive technological developments has been additive, (i.e., the knowledge inherent in one advance has been incorporated in each succeeding development).

In past ages, the rate of change of technology development has been relatively slow, taking many decades to complete and be incorporated into worldwide society. Figure 1 shows, however, that during the last 40 years, the rate of technological change has increased dramatically. The result of this almost explosive rate of change is that new technological developments are introduced and, in some cases, replaced within a few decades with even more advanced concepts.

This rapid change in technology coincides with the development and growth of the electronic ceramics industry. In fact, man's ability to manipulate and control the electronic properties of ceramic materials has played a major role in our transformation from the Steel Age to the Information Age and our transformation from local economies to a world economy. Nearly instantaneous satellite communications from coast to coast and around the world would not have been possible without simultaneous advances in semiconductors, dielectrics, ferroelectrics, ferrites, and opto-

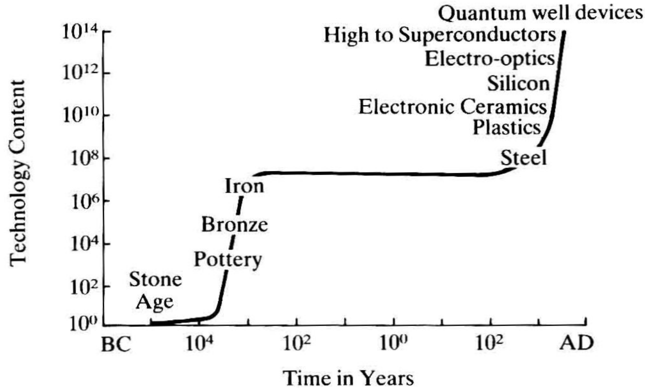

FIGURE 1. The evolution of materials.

electronics. The continued developments in these fields are being matched, and perhaps eventually superseded, with advances in superconducting ceramics, photonics, optical waveguides, and potentially even optical computing and information processing.

It is difficult to establish a realistic historical date for the origin of electronic ceramics as a field. Development of the technology for evacuation and sealing of glass envelopes for incandescent lighting and vacuum tubes dates back a century. Porcelain ceramics have been used for electrical insulation from the beginning of the electrical industry, also a century ago. The discovery of ferrimagnetic behavior in iron oxide spinels by Snoek occurred as long ago as 1919, and ferroelectricity was observed in Rochelle salt as early as 1921.

However, the field of modern electronic ceramics, as presently known, is primarily based upon the specialty electronic materials developed since the 1940s. These materials, such as barium titanate, developed by von Hippel in 1945, were optimized for specific electronic characteristics by controlling their composition and microstructure. Equally important, the successful engineering of new electronic materials was accompanied by the development of solid-state physics and an atomistic level of understanding of the physical principles responsible for the improved performance of the materials.

The objective of this book is to describe the physical principles of this broad class of electronic materials. It is an exciting challenge, since the range of properties of electronic ceramics is the largest known, from the highest electrical resistance to the lowest. The origin of their differences derives from variations in the electronic bonding and the atomic structure of the materials. Consequently, the book begins with a review of the structural concepts of ionic compounds and amorphous solids (Chapter 1) followed with a development of quantum mechanics and electronic bonding which leads to energy band theory (Chapter 2).

The description of semiconductor properties (Chapter 3) is based upon energy band theory and electron transport. Comparisons are developed between low-band-gap Si and GaAs semiconductors with a high-band-gap semiconductor, SiC. Also, the theory of amorphous semiconductors is compared with that of crystalline semiconductors.

Ionic conductivity is described in Chapter 4, with application to both insulators and fast ionic conductors. Crystal compound semiconductors that possess both electronic and ionic defect structures are also treated in Chapter 4.

The theory of linear and nonlinear dielectrics is presented in Chapters 5 and 6, with emphasis on the structural mechanisms of the electric field dependence of these materials. Applications to several important commercial ceramic insulators and ferroelectrics are described.

Magnetic ceramics (i.e., those exhibiting ferrimagnetism) are discussed in Chapter 7. The optical properties of glasses and crystalline ceramics are described in Chapter 8 in terms of the interaction of photons of a characteristic energy, or wavelength, with the electronic and ionic structure of the material. Use of ceramics and glasses to guide light is the subject of Chapter 9. The switching of light by various optically active ceramics is the subject of Chapter 10, and light amplification by simulated emission of radiation, or lasers, is developed in Chapter 11. Finally, the theoretical and structural basis of the newest class of electronic ceramics, the high-T_c superconductors, is presented in Chapter 12.

Throughout this volume we have attempted to describe the theory in structural terms, using quantum mechanics or statistical mechanics as an aid, but not an end in itself. Thus, this text is designed to fit in the gap between a solid-state physics text, where the emphasis is entirely on theory, and a ceramics or materials science text, where the emphasis is largely on processing and microstructure. Nearly all equations are derived, and where possible from first principles. Some applications of the theory are given in each chapter with a description of the relevant properties of a range of materials. However, with no apologies, this volume is not a handbook of electronic ceramics. There will obviously be many useful materials excluded from the various tables and figures. An ample reading list is provided though, for the serious student, scientist, or engineer who wishes to explore the subject more deeply or find additional property data.

Throughout the book we adopt the convention of the American Ceramic Society, where glasses and amorphous solids are considered as a subset of the generic field of ceramics, defined broadly as inorganic-nonmetallic materials.

For the student and serious reader, we have attempted to present a useful set of calculational problems for each chapter. We hope to advance the depth of understanding through some of the problems in each set. Consequently, several are quite difficult. Also, at least one problem per set requires use of a computer to do it properly. This is an effort to aid the student in preparation for the "real world," where compositional tailoring of the properties of electronic ceramics are commonplace and one of the great strengths of the field. An answer key is available for instructors or nonstudent readers.

The level of the text is for a senior in an engineering or science curriculum or first-year graduate student. It is assumed that the reader has had at least an introductory course in materials science, knows the rudiments of crystallography, and understands the difference between single crystal, polycrystalline and amorphous materials. For the reader without this background, Chapter 1 provides a brief review. We also assume the reader has some knowledge of thermodynamics, phase equilibria, and phase transformations. The reader also should understand calculus with at least a modest background in differential equations. Our goal is to prepare reader to explore the literature in this exciting and enormously rewarding field. There are thousands of research papers published annually concerning the materials covered in this volume. They all assume an understanding of the concepts presented herein. We hope this book will open the door to this rapidly growing library of information.

In order to enhance clarity we have chosen to minimize reference citations within the text. The reading lists have been chosen to satisfy most needs for additional references. We hope the many researchers who have contributed to the scientific development of electronic ceramics will forgive us for not mentioning them by name.

Finally, we wish to acknowledge the continued spirit and enthusiasm for research and teaching in the University of Florida Department of Materials Science and Engineering and a great group of graduate students over the years, which provided the incentive for producing a text such as this. The assistance of Frank Cerra and Carol Beasley at John Wiley has also been invaluable. The continued intellectual and research support of Don Ulrich and the Air Force Office of Scientific Research has also been highly important to us for a long period of time. A very special acknowledgment is noted for the assistance of Alice Holt throughout this project for her management and secretarial leadership, and Minnie Stalvey for her typing.

L. L. HENCH
J. K. WEST

Gainesville, Florida
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INTRODUCTION

1.1 OVERVIEW

Electronic ceramics originated as speciality electrical insulators made by the ceramic whitewares industry. The need for progressively higher performance sparkplugs for automotive and aircraft engines during World War II provided the motivation to improve the traditional clay–feldspar–flint triaxial porcelain body widely used in housewares and for low-voltage insulation. Removal of the ionically conducting potassium ions from the insulator composition was achieved, leading eventually to an all-alumina body and the beginnings of high performance molecularly tailored electronic ceramics.

Development of ferroelectric and piezoelectric components occurred at the same time, also utilizing the new concept of solid-state sintering for densification of the materials. Solid-state sintering provided the advantage of eliminating the ionically conducting, glassy grain boundary phase which results from liquid phase sintering or vitrification. Consequently, the physical properties of the new electronic ceramics were dependent solely on an assemblage of polycrystalline phases and a very small amount of residual porosity.

However, in order to achieve a high-density sintered compact without use of liquid phase sintering, it is essential to control the purity and size of the starting powders, their size distribution, and extent of agglomeration. Without such processing controls the fired ceramic can possess a broad range of grain sizes and porosity, and uncontrolled grain boundary phases. These can degrade the physical properties and increase the environmental sensitivity of the ceramic component. Variability in properties and