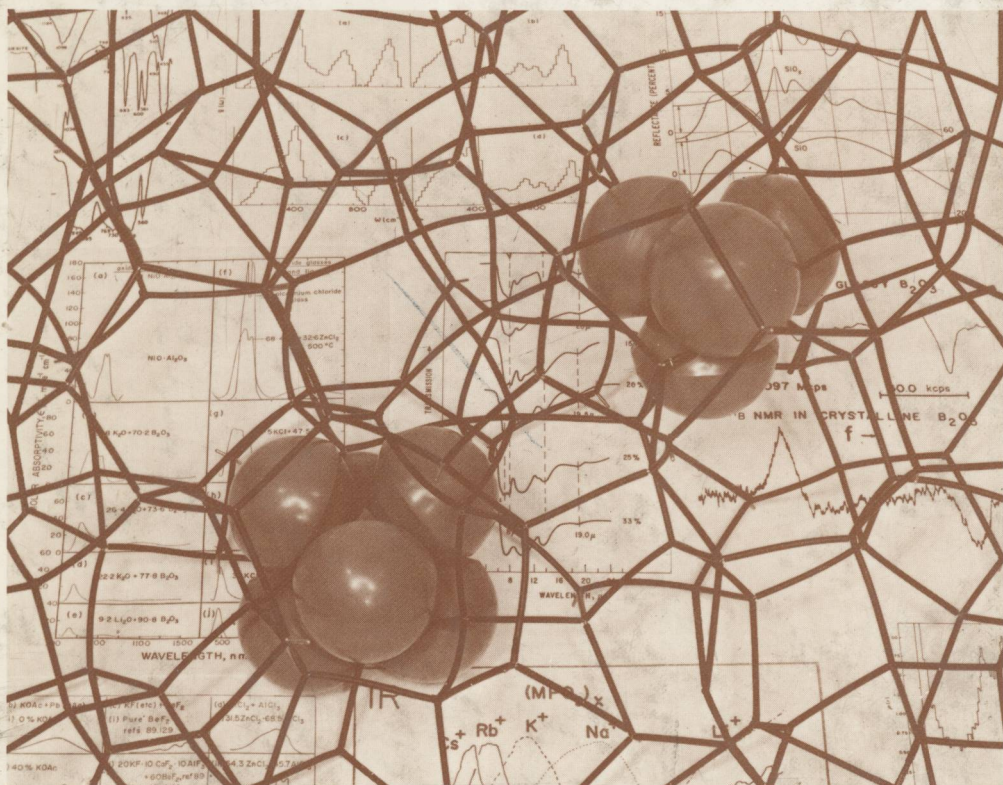


**J. WONG**  
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# GLASS

## Structure by Spectroscopy

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MARCEL DEKKER, INC. New York and Basel

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MARCEL DEKKER, INC.

270 Madison Avenue, New York, New York

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 76-11104

ISBN: 0-8247-6468-4

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

To our families

Mei, Glenn, Christina, and Theresa Wong

Iris, Austen, Sonia, and Sandra Angell

for their patience and understanding.

## PREFACE

The need for a monograph in the area of spectroscopic investigations of the vitreous state of matter became apparent to us during the preparation of a review of recent progress in this area. Various monographs on investigations in specific spectral regions may refer briefly, usually very briefly, to the characteristics of vitreous materials vis-à-vis their crystalline counterparts: or, books on the glassy state may use selected spectroscopic results to support an argument; but at the moment there exists no book devoted to the general area of spectroscopy of glassy materials, despite the very large number of research papers on various specific aspects of the subject. In view of the currently increasing interest in the vitreous state of matter, and of the power of spectroscopy to provide details not only on local structure of glassy materials but also on the particle dynamics of the state, the lack of a book devoted to spectroscopy in glasses is unfortunate. It is our desire that this volume should go some way towards filling the gap, and at the same time provide various vitreous state spectroscopists as well as newcomers in the field with a general, but coherent, view of the subject.

The field of spectroscopy is very broad. Not only is the basis of the radiation-matter interaction, which leads to energy dissipation in specific spectral regions, often subtle and incompletely understood, but the instrumentation needed to observe the interaction and measure its magnitude accurately is frequently complicated and fraught with problems which should be thoroughly understood before conclusions on the proper significance of the measurement are drawn. The authors are cognizant of the audacity involved in attempting to cover this whole area, since it is clearly not possible to become expert in all its aspects. We expect to make some errors in judgment,

and hope that those whose knowledge and understanding in different areas exceeds our own will be tolerant of such errors. We consider the object of bringing together, in some consistent way, information on the glassy state from a wide range of investigations is sufficiently worthwhile to warrant the embarrassment of exposing our own limitations in different specialized areas. Thus we begin with an apology, hoping the reader will understand our difficulty, and will find something of value in the compendium of information presented.

In order to provide some connecting threads for the rather complex fabric of spectroscopic results we will discuss in this book, we have included an introductory chapter which reviews general properties and phenomenological characteristics of the viscous liquid and glassy states, and the transition between them. To balance the emphasis on structure and bonding which is inevitable in a book on spectroscopy, this initial chapter will be mainly concerned with a discussion of those features which are common to all glasses and which, as much as long-range disorder, define the glassy state.

Although the elastic scattering of x-rays, neutrons or electrons is strictly not a branch of spectroscopy insofar as radiation is diffracted rather than absorbed or emitted, recent diffraction studies such as small angle x-ray scattering (SAXS) in phase-separated glasses and further refined radial distributions analyses beyond the next-nearest-neighbor coordination sphere by eliminating Compton scattering at high values of  $\sin \theta/\lambda$ , will be covered in an early chapter because of their great importance in structural investigations at both the atomic as well as microstructural levels of glassy materials. To emphasize the usefulness of model construction in its role of elucidating experimental diffraction data of amorphous solids, current structural studies and radial distribution analyses of amorphous semiconducting Si and Ge as well as some simple binary and ternary amorphous metallic alloys have also been included in the diffraction chapter.

Vitreous thin films formed by vapor deposition have aroused considerable interest in recent years. These films may be insulating or semiconducting, and play an important role as diffusion sources,

diffusion masks, passivation layer, etc...in the planar technology of fabricating microelectronic devices and circuits or serve as major construction materials for xerographic, memory and threshold switching devices. Spectroscopy, especially in the UV and infrared regions, is a very powerful tool for probing the structure as well as characterizing the physico-chemical properties of these vapor-deposited materials. In the case of binary silicate glasses, chemical bonding in these vapor-deposited dielectrics, film composition and thickness can quantitatively be determined in a nondestructive manner from their infrared transmission spectra. Of particular interest is the use of thin films for differential spectral measurements which, in the case of vapor-deposited phosphosilicate glasses, enable broad absorption features to be resolved in the fundamental vibrational region. Such resolution is usually not possible with bulk specimens because of the high absorption coefficients ( $10^3$ - $10^4$   $\text{cm}^{-1}$ ) of band maxima in silicate-based glasses. It is, therefore, our desire in the present endeavor to bring to the attention of vitreous-state workers the properties of the corresponding thin film studied by thin-film workers and vice-versa, so that meaningful property correlations between the thin film and bulk material may be obtained and better insight into the structure of the vitreous state may result.

Although spectroscopy is most readily seen as contributing to knowledge of structure and chemical bonding in glassy materials, it should be recognized that as one goes to lower and lower frequencies the spectral band shape is more and more strongly influenced by time-dependent properties of the absorbing medium. Apart from the fields of EPR and NMR spectroscopy, the use of absorption spectra to obtain information on irreversible phenomena is rather recent. Since structural relaxation, and the "freezing-in" of a particular configuration at the glass transition, are such a vital part of the overall "picture" of the glassy state, it is important to consider the role spectroscopy can play in the elucidation of relaxation processes. Although these processes can only be studied at very short relaxation times (high fluidities) using the radiant energy source and detector systems of conventional spectroscopy, it is possible, by utilizing

bridge techniques, to measure parameters related to dissipation of the energy of an oscillating electrical field to very low frequencies, e.g. in dielectric relaxation. Taken together, and including frequency-dependent mechanical energy loss studies, such measurements define a research area which may be termed "relaxation spectroscopy," to distinguish it from "resonance spectroscopy." Since such studies are quite essential to the elucidation of mass transport processes in glass-forming materials, we believe it is fitting to include a chapter under this title in the present book.

In this book, we have preferred to adopt as basis for order of presentation the energy of the absorbed or emitted photons involved in the study. Thus spectral topics will be discussed in the order: Mössbauer spectroscopy, extended x-ray absorption fine structure, UV absorption spectra, visible absorption and fluorescence spectra, IR and Raman spectra, and EPR and NMR spectral studies. The Relaxation Spectroscopy chapter will be placed at the end because of the different character of these studies. Under each topic we will consider, in this order, fundamentals and general aspects of each branch of spectroscopy, new utilizations of the spectral region, new instrumentation or techniques for application of the branch of spectroscopy to studies of glasses, outline of current theoretical treatment of the spectral observations, and finally investigations of different chemical systems by established techniques, and their interpretations.

The order chosen for discussion of spectral studies on different glass-forming chemical systems is one of movement from left to right and top to bottom along the periodic table for the principle network-forming cation, i.e. borates before silicates before germanates before phosphates before arsenites before other oxide systems before chalcogenide glasses, followed by whatever other systems that may have been studied, e.g. glassy and molten salts, for which the number of studies are insufficient to justify further breakdown according to chemical constituents.

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## ACKNOWLEDGMENTS

A number of substantial improvements in accuracy and clarity in the monograph have been offered by our colleagues in various disciplines. In particular, we are indebted to A. Barkatt and C. T. Moynihan for their valuable discussions and critical readings of Chaps. 6 and 11, respectively. Among others who have been kind enough to review individual chapters and offer advice and specific comments are

|              |                   |              |              |
|--------------|-------------------|--------------|--------------|
| P.J. Bray    | M.D. Ingram       | H.R. Philipp | S. Urnes     |
| M. Goldstein | N.J. Kreidl       | W.A. Pliskin | G.D. Watkins |
| D.L. Griscom | W. Müller-Warmuth | D.E. Polk    | A.C. Wright  |

Permission by various Journals and Publishers to reproduce published figures and illustrative diagrams is acknowledged accordingly in the appropriate sections of the text.

One of us (J.W.) would like to thank the General Electric Corporate Research and Development for providing the atmosphere and necessary facilities for this work. C.A.A. has benefited from the support of the National Science Foundation and the GTE Research Laboratory. Manuscript preparation and secretarial assistance by S. K. DeMeis, C. Ladu, J. Quesnel, J. Redelman, B. Rile, and H. Ruth are gratefully acknowledged. The final manuscript was typed with the able assistance of A. Kotiranta.

J. Wong  
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## Chapter 1

### THE VISCOUS LIQUID AND GLASSY STATES: GENERAL ASPECTS

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#### 1.1 INTRODUCTION AND DEFINITIONS

The glassy state is a non-equilibrium state of matter which, as recent studies of lunar surface materials have shown, may persist over truly cosmological periods of time. Such patent violations of the ergodic hypothesis provide a challenge to the theoretician and experimentalist alike. It is with the elucidation of some aspects of the glassy state problem that this book is concerned.

In this initial chapter we consider general aspects of the problem, particularly the relation between crystal, glass, and liquid states, before passing on, in later chapters, to the details

of structure and dynamics of glasses which may be revealed by spectroscopic studies.

Since the terms "vitreous", "glassy", and "amorphous" are used with somewhat different connotations by different authors, we should first of all clarify, for the purposes of this book, what we understand these terms to mean. The term "amorphous" we take to be very general and, consistent with its Greek roots, to be descriptive of any condensed phase which lacks long-range order according to diffraction (x-ray, neutron and electron) criteria. Thus liquid mercury and carbon black are equally representative of the amorphous state of matter. "Glassy" and "vitreous" we consider to be synonymous and to be descriptive of a very restricted class of amorphous materials, viz. those which not only are solid as judged by mechanical criteria but which have particular "glassy" characteristics as follows. A useful definition of what constitutes a glass has been given by the National Research Council Ad Hoc Committee on Infrared Transmitting Materials [1]. They suggest a glass is an x-ray amorphous solid which exhibits the glass transition, the latter being defined as "that phenomenon in which a solid amorphous phase exhibits with changing temperature a more or less sudden change in the derivative thermodynamic properties, such as heat capacity and expansion coefficient, from crystal-like to liquid-like values. The temperature of the transition is called the glass (transition) temperature and denoted  $T_g$ ." It should be noted that in the case of a small class of highly stable inorganic glasses, the magnitude of the changes observed may be very small and not easily observed.\*

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\*The exact temperature at which these changes are observed to occur depends on the type of measurement used to detect them. If the measurement is performed slowly, e.g. over a period of several minutes, then the property changes will be observed to commence at a significantly lower temperature than if the measurement is performed very quickly. This is because the changes of thermodynamic properties are dependent on changes in internal structure of the amorphous phase, which occur slowly near  $T_g$ . The glass transition phenomenon is observed when this "structural relaxation time" becomes commensurate with the time scale of the experiment. Because this structural relaxation time also determines the magnitude of the liquid



This definition has the advantage of restricting the term "glass" to materials which are capable of existing under certain circumstances in a state of internal equilibrium (above the glass temperature, or glass transformation range), and thus to materials which may be obtained in reproducible states despite extensive temperature cycling. This restriction bestows on glasses a certain respectability not available to many amorphous substances, e.g. to the majority of vapor-deposited amorphous solids. The definition does not restrict the term "glass" to materials formed by continuous cooling from the liquid state; rather it includes materials formed by dehydration [2], vapor deposition [3], chemical- or electro-deposition [4], and shock treatment [5].

Above the glass temperature, the amorphous phase has the thermodynamic properties of the liquid state, hence is referred to as being in the "supercooled liquid" as distinct from the "glassy" state. As will be clear from the more detailed discussion given later, there is some arbitrariness in these distinctions since whether an amorphous phase exhibits liquid-like or solid-like behavior depends on the time scale of the experiment which measures that behavior. Generally, in distinguishing supercooled liquid from glassy behavior one has in mind experiments on time scales of seconds or minutes.

There are, unfortunately, a number of interesting and probably important borderline cases of rapidly quenched liquid- or vapor-deposited materials that appear to have all the structural and dynamic properties of glasses but which, lacking kinetic stability in the amorphous solid state, crystallize during heating before attaining the supercooled liquid condition. The authors can, however, see

---

state viscosity, the glass transition temperature is usually associated with a particular value of the viscosity. The popular idea that  $T_g$  is the temperature at which the liquid viscosity reaches  $10^{13}$  poise is based on thermodynamic measurements (density, refractive index) carried out on time scales of many minutes. If  $T_g$  is detected using a faster method, e.g. differential thermal analysis, then the viscosity at  $T_g$  would be closer to  $10^{11}$  poise. This matter is discussed in more detail in the later section of this chapter and is very much central to the subject matter of Chapter 11.