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Glasses and the vitreous state

Translated from the French
by
William D. Scott and Claire Massart

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Foreword

These remarks are to introduce the first text on the science of glasses to be published in the Cambridge Solid State Science Series since its beginnings 17 years ago. The absence of such a book hitherto is not a reflection on the editors' judgment as to the importance of the field – far from it! It reflects, instead, the fact that good general books on glasses are few and far between; they are certainly less numerous than good books on metals, ceramics, semiconductors or composites. This paucity of glass books can hardly be due to an undervaluation, by the materials community, of one of the most venerable classes of material in human civilization which has also been the focus of intensive modern research. One must conclude that good glass books are rare because they are particularly difficult to write.

I have had the good fortune to know Jerzy Zarzycki for many years past; our first meeting was due to a shared passion for materials science, at that time a novel concept. Prof. Zarzycki has been both an industrial research director and the director of a university glass research laboratory and he is a linguist and an indefatigable traveller among the purlieus of glass research. His view of the field is accordingly a comprehensive one, and this showed very clearly in his French text, *Les Verres et l'Etat Vitreux*, which appeared in Paris in 1982. As soon as I read this, I realized that here was a text that should be made available to anglophone scientists. The practicalities of arranging for this, including revision, expert translation and all the necessary permissions, necessarily stretched over years, and so it is only now, in 1991, that the English version can be presented to the public. Readers can however be assured that every care has been taken to ensure that the subject-matter remains up to date.

The field of glass science is so extensive that no single-volume text can cover every facet in equal detail. This book takes a broad view and emphasizes aspects of glass science that are general to all, or most, kinds of glasses, in preference to detailed presentation of the properties of particular categories of glass. Thus, topics like the glass transition, tendency to glass formation, rheology, optical characteristics, and the many features of glassy structure, are examples of those which are thoroughly treated here. Attention is also devoted to the modes of glass production, including especially the modern sol-gel process to the development of which Prof. Zarzycki has made major contributions.

I am particularly pleased that the Cambridge University Press can in this transparent way make its contribution to the cross-channel and transatlantic *Entente Cordiale*.

Robert W. Cahn
1990

Introduction to the English edition

Glasses constitute a fascinating group of materials both from the fundamental and applied standpoints. They are among the most ancient materials in human history and it seems paradoxical that our knowledge of their structure is far from being complete.

To the fundamentalist, glasses present the challenge of studying disordered solids which lack the spatial periodicity typical of crystals. Most of the standard interpretative methods are less effective or inapplicable and the description of the structure is limited to statistical approaches. This explains why it is only recently that the structure of glasses has begun to be better understood thanks to the simultaneous application of ever more sophisticated investigation methods.

The very existence of this type of condensed state of matter brings about difficult thermodynamic and kinetics problems which are not as yet completely resolved.

In spite of these difficulties Glass Science has made decisive progress in the last three decades and significantly in the sixties which represent the "golden age" of glass research. During this period our understanding of glass and the vitreous state experienced truly explosive growth similar to that in metallurgy a few decades earlier. Glass is no longer solely a material of primary technological value for architecture, transport, lighting or packaging. New types of glass have been discovered and these play an increasing rôle in modern optics (lasers), electronics, opto-electronics, energy conversion and in medicine (bio-materials). Glass has been promoted to the rank of a noble material, not only for "passive" but also for "active" applications. New modes of synthesis have been developed, e.g., the "sol-gel" approach in which the "wet" methods of colloidal chemistry replace the traditional high-temperature routes used in glass melting.

Glass science thus encompasses all the different aspects found in materials science and necessitates a knowledge of the various fields of physics, chemistry and mechanics.

The book *Les Verres et L'Etat Virtreux* was written in 1979, to meet teaching needs in France and to serve as a homogeneous introductory course to the various aspects of the physical chemistry of glass. It was the first textbook in French on this subject and was addressed primarily to students in universities and engineering schools confronted with the problem of glass in their materials science curricula. However, it also contained sufficient bibliography to be of interest to researchers entering this field. In response to many requests by English-speaking scientists this work has now been translated into English.

The bibliography has been thoroughly updated and additional information provided on several types of glasses. Because of their ultra-low attenuation, halide glasses are now potential candidates for optical fibers and are also particularly important for their exceptional optical characteristics which make them suitable for high power lasers in thermonuclear fusion experiments.

Metallic glasses, which are obtained by ultra-fast quench of liquid metal alloys, have shown a very rapid development because of their interesting properties which earned them the name "materials of the century" in the USA and "dream materials" in Japan. They are used in many electronic devices, in particular in audio-video techniques.

The "precursor-based" synthesis of glasses, ceramics and composites is, at the present time, one of the most rapidly progressing fields of material science and engineering. The "sol-gel" method of preparing glasses is being actively studied in leading laboratories all over the world and, in the last ten years, the number of scientific publications in this field has shown an exponential increase. This warranted an additional chapter on this subject for the present edition.

The book is divided into several parts:

Chapters 1–7 present aspects of the *vitreous state* in general. A knowledge of physics, chemistry and thermodynamics and, in particular, the theory of equilibrium diagrams is a prerequisite. The possibilities of applying various methods of studying the structure of disordered systems are concisely treated and references to appropriate monographs giving more details are indicated.

Chapter 8 presents the *classification* of various systems of practical importance.

Chapters 9–16 describe different properties of glasses considered as *materials*. Rheology (Chapter 9) and brittle fracture (Chapter 14) are treated more extensively because of their importance in glass science and technology.

Chapter 17 gives a condensed summary of *glass production techniques*. These are important even for readers who are not technologically inclined, as they determine the final characteristics of the materials obtained in practice.

Chapter 18 describes new glass-making processes based on the sol-gel approach from precursors.

Because of the vastness of the subject and the limited space available, the presentation had to be substantially condensed and, unfortunately, certain subjects had to be omitted. However, the bibliography will permit readers access to more specialized sources of information where necessary.

I wish to thank Professor William Scott of the University of Washington and Ms Claire Massart, Seattle, Washington for their excellent translation. My sincere thanks also go to the Corning Glass Co. and the Saint-Gobain Co. for the interest they have shown in this venture and for providing several original micrographs. Especially I would like to take this opportunity to acknowledge the late Dr. Ivan Pechès who first introduced me to the exciting intricacies of glass structure. Finally my greatest thanks go to my wife, Margery, for her many painstaking readings of both the French and English manuscripts and for her constant encouragement.

I hope that this work will be a useful guide to all those who are interested in the Science of Glass.

J. Zarzycki
Montpellier, 1990

Historical overview

Glass is one of the most ancient materials known to mankind. In prehistoric times, *obsidian* was used to make knives, arrow tips etc. from natural glass originating in Europe, mainly from the islands of Melos and Thera in Greece. The most ancient *glass* objects made by mankind were discovered in Egypt and are dated approximately 3000 BC. However, methods of manufacturing glass had already been discovered in Mesopotamia by approximately 4500 BC.[21]

This glass consisted essentially of a $Na_2O–CaO–SiO_2$ composition close to that of modern industrial glasses. It was obtained by melting together sand with alkaline flux from sea plant ashes or from minerals such as soda ash.

The use of glass as a material *per se* was preceded by the use of *enamels* on pottery, some of them dating from 12000 BC. The origins of this discovery remain unknown. Pline stated the possibility of an accidental vitrification of sand by reaction with soda ash blocks in a primitive Egyptian fireplace. It is more likely that the first glasses were simply slags from copper metallurgy.

Glass was first used as pieces cut into beads and other jewels (mummies' eyes were made out of obsidian). Glass containers were made during the reign of Touthmosis III (fifteenth century BC). They were obtained by forming a sand core coated with a potassium salt and then superficially vitrified. After cooling, the core was removed by scraping, leaving a rough internal surface. Egyptian vases were decorated in a very similar way to the vase discovered in the Ur excavations. The glass industry flourished in Egypt up to the twelfth century BC; then in Syria and Mesopotamia, until the ninth century BC. The glass products were distributed by the Phoenicians. Glass centers appeared in Cyprus, Rhodes and Greece, on the Italian peninsula (about 900 BC) and in the region around Venice (500 BC). Manufacturing techniques evolved: vases were fabricated from glass rolls (often multicolored) formed around a central core of sand then melted together. Glass pieces were also used to obtain mosaics by sintering, a technique called *"millefiori"*.

After its conquest by Alexander The Great, Mesopotamia declined and Alexandria in Egypt became predominant. New techniques were imported from Italy around 100 BC and the Syrians established new manufacturing enterprises by the beginning of our era.

Glass blowing was probably invented in Phoenicia (around 50 BC) and certainly revolutionized forming techniques by eliminating the use of a central core. This technical development stimulated art glass which spread from Persia to the Orient. In the Western world, the existence of the Roman Empire helped in establishing numerous glass centers; Syrian and Alexandrian glass blowers were working in Rome and the provinces of Saône and Rhine; the art then reached Spain, the Netherlands, Gaul and Brittany. Glass prices reduced considerably so that the use of blown glass containers became popular. Flat glass for window panes was practically unknown although excavations of Pompeii showed a few samples dated from the beginning of our era.

After the decline of the Roman Empire, refugees brought the art of glass blowing to the area around Geneva and it then spread all over Europe. Techniques hardly changed up to the eleventh century. The ashes of sea plants containing sodium were replaced by those of earth plants containing potassium.

The art of coloring glass was stimulated by the Church (stained glass).

The importance of Venice as a glass manufacturing centre grew steadily from the tenth century onwards. Murano became a large glass center where "Venice crystal" was made. Commerce with the Byzantine Empire lasted until the fall of Constantinople; interest then turned to the Western world and, until the end of the seventeeth century, Venice was predominant in the world of glass. Some groups worked first in Lorraine and Normandy, and then moved to England where coal furnaces were introduced in the seventeeth century.

The book *Arte Vetraria* by Neri published in Pisa in 1612 gives an overview of the knowledge of glass available at that time and was translated into many other languages. In Bohemia, "crystal glasses" were developed which had a particular brightness due to a high level of lead oxide.

In France, official control over the glass industry began in the sixteenth century. Henry IV conferred exclusive rights (lasting from 10 to 30 years) on Italians who were allowed to manufacture glass in several cities such as Paris, Rouen, Orleans and Nevers. Starting in 1665, Colbert made a centralised glass industry by creating a flat glass industry to produce the mirrors for the Palace of Versailles. The Saint-Gobain factory, created on the initiative of Colbert to fight the Venetian monopoly, became the Manufacture Royale des Glaces de France in 1693. France then surpassed Venice as an exporting country for mirrors. The Baccarat factories (crystal glass production) were founded in 1765.

By the end of the eighteenth century, an industrial revolution took place as a result of chemical discoveries based on the replacement of natural alkali by sodium from sea salts, obtained first by the Leblanc technique, then in 1863 by the Solvay process.

Deslandes (Saint-Gobain Co.) showed the importance of adding limestone to glass to give it chemical durability. This addition was made necessary because natural ashes which provided part of the lime had been replaced by very pure alkalis from the chemical industry.

By the end of the nineteenth century, mechanized forming processes were introduced (see Chapter 17 on technology). The invention of continuous glass drawing procedures for window glasses as well as the manufacture of plate glass were followed by the introduction of continuous casting on the surface of a bath of molten tin (the "FLOAT" process) in 1955–60, a revolution for the glass industry.

Together with technological improvements, a better understanding of the physical and chemical properties of glass emerged due originally to the use of optical glass. Glass lenses were known by the Greeks who passed their knowledge on to the Arabic world. Eye glasses were made in 1280 in Italy and the first telescope lenses were fashioned in Italy and the Netherlands around 1590. (The telescopes of Galileo and Kepler date from 1609 and 1610 respectively.) Until the end of the eighteenth century, optical glasses were treated as a sub-product of the ordinary glass industries, the glass used for this latter purpose being of poor quality. A definite improvement was obtained at the end of the eighteenth century by Guinand in Switzerland, who introduced stirring of glass to ensure good homogeneity. Working together with Fraunhofer, he widened the range of crown and flint glasses (see Chapter 12). A diversification of glass production took place by systematically introducing B_2O_3, P_2O_5 and a number of other oxides thanks to the collaboration of Abbe, Schott and Zeiss in Germany at the University of Jena around 1875. New glasses could then be produced and, within a period of ten years, progress was spectacular. Zeiss maintained a monopoly in the optical field, in particular for microscopes, up to the First World War. Starting from this period on, Parra-Mantois in France, Chance Brothers in Great Britain and Bausch and Lomb in the United States developed a competitive industry. Around 1917, Adams and Williamson resolved the problems of glass annealing and also rare earth oxides were introduced in the compositions.

Thus, the scientific approach was progressively introduced. The systematic measurement of the physical properties of various glasses was started around 1920 in Great Britain under the direction of Turner at the Department of Glass Technology at the University of Sheffield. As a result, a slow but steady generalization of the concept of glass took place and the term glass began to be applied to define a non-crystalline solid in general, not only an oxide glass. Tammann's studies in 1930 confirmed this point of view by directing research toward a general understanding of the *vitreous state* as a state of aggregation in matter. The approaches which were first of a purely phenomenological nature were then slowly directed toward more and more structural studies.

But only after the Second World War do we see strong interaction between scientific research and glass technology. In fact, the period 1950–60 can be considered as the blossoming period of true glass science. In France, glass science progressed rapidly due to the inspired guidance of Ivan Peychès, Director of the Research Laboratories, Saint-Gobain Co. All modern methods in physics and chemistry have been successively applied to the study of glass and the effort in this direction has intensified as we can see through the numerous scientific and technical works issued by different laboratories and research centers throughout the world.

Besides classical applications, in which glasses are indispensable to modern economy (construction, transportation, lighting, chemical industry etc.) we can see new glass techniques appearing (lasers, optical fiber communications, energy transformation) where glass brings original solutions.

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