HIGH - PERFORMANCE
GLASSES

Edited by
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BLACKIE

Preface

Glass has been manufactured for thousands of years, and in the early days was used to make jewellery and highly-prized jars. Today, hand-cut lead crystal glass is valued for its refractive properties, and soda–lime–silica glass is used to make containers and most of our windows. Among the special properties of glass, ease of fabrication, optical and electrical properties, chemical durability and hardness are those most relevant for the majority of modern-day applications. Without glass, the growth of the geological, biological and materials sciences (with their heavy reliance on optical characterization) would have been impossible. Design for selected electrical applications has always been important, and the early electronic and lighting industries would not have succeeded without the availability of high resistance, impermeable glass envelopes for the protection of the sensitive internal components.

Modern society has created a demand for a whole new range of glass products for use in information transmission, signal processing, energy conservation (plus generation and storage), waste encapsulation, and healthy living in hostile environments. In this book the early chapters are concerned principally with glass fabrication while the later chapters concentrate on the development of glasses for particular applications. Following a brief introduction (chapter 1), chapter 2 provides an overview of the very active field of sol–gel glass production, which increasingly has widespread applications in many fields, including coatings, optical fibres, doped glasses, catalysis, microballoon fabrication and transparent insulating glasses. Chapter 3 looks at the manufacture of nitrogen-rich glasses and the corresponding improvements in physical properties. A major current field of activity is the modification of glass properties by coatings, and this is the subject of chapter 4, the main emphasis of which is the use of coatings in the architectural field. Chapter 5 describes the fabrication of very thin glass sheets to accurate tolerances for optical display panels. Chapter 6 covers glass ceramics, which have the advantages of ease of fabrication (as for conventional glasses) combined with the improved strength properties of fine-grained, non-porous ceramics.

Chapter 7 describes ionically conducting glasses, and is followed by a group of chapters concerned with variable glass durability: chapter 8 discusses bioactive glasses and provides a view of the developing field of materials for medical applications; chapter 9 describes the soluble glasses which provide a valuable source of trace elements in the diet of

ruminant animals feeding on marginal pasture lands; and chapter 10 analyses the development of glass as a storage medium for radioactive waste disposal. The last four chapters of the book are concerned with optical applications, always a major field of activity for glass technologists. Glasses used for optical non-linearity in the presence of high-intensity light beams are discussed in chapter 11, and special optical elements such as gradient-index lenses (particularly important in developing optical processing systems such as compact discs) are discussed in chapter 12. Glasses which have been developed for their exceptional infrared transmission are described in chapter 13. Finally, chapter 14 describes the photostructural characteristics of chalcogenide glasses and considers the possibilities of fabricating optical elements such as diffraction gratings and Fresnel lenses on a fine scale.

This book is intended as a stimulant to the development of further areas of glass technology; we hope that it will be a valuable source of reference and a teaching resource for advanced students and research workers. We look forward to the many future developments in the applications of glass which are as novel and varied as those described here.

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1 High-performance glasses

M. CABLE

1.1 Introduction

A widely used definition says that a glass is an inorganic product of fusion which has cooled to a rigid state without crystallizing. Although this definition, originally adopted about sixty years ago for commercial rather than scientific reasons, is open to some objections, it contains the essential features by including information about both structure and properties. Glasses are materials which have amorphous or liquid-like structures but which behave as solids at low temperatures. A glass scientist generally considers the crucial demonstration to be that a glass shows *transformation range* behaviour or a *glass transition*. This is a particular kind of *reversible* behaviour in a narrow range of temperatures within which the transition from liquid to non-crystalline solid occurs on cooling (or the converse on heating). Within this interval, which is characterized by one temperature always called T_g, properties depend on thermal history, not just current temperature, and properties can be observed to change with time. This happens because the transformation range is the temperature range over which structural relaxation times are measurable, the limits being that they are too short to measure at the upper end and too long to detect at the lower end. Within this range, density, viscosity, electrical conductivity, heat capacity, and so on can be changed reversibly by suitable heat treatment but different properties involve different mechanisms of relaxation and the value of T_g depends on the particular property being used to measure it. The values of properties at lower temperatures can thus be varied to some extent by controlling the rate of cooling: rapid cooling 'freezes in' a structure that would be in equilibrium (as a glass) near the upper end of the transformation range while very slow cooling will give a structure that would be in equilibrium at a lower temperature.

Figure 1.1 shows the most common way of visualizing these effects by considering how the volume of a melt may change when cooled at different rates. The room-temperature density of the glass can clearly be affected by its heat treatment. Density and refractive index are related, showing why optical glasses, which need refractive index to be constant within one lens element to about 1 part in 50 000, need *fine annealing* to give the whole slab the same thermal history, not merely to relieve
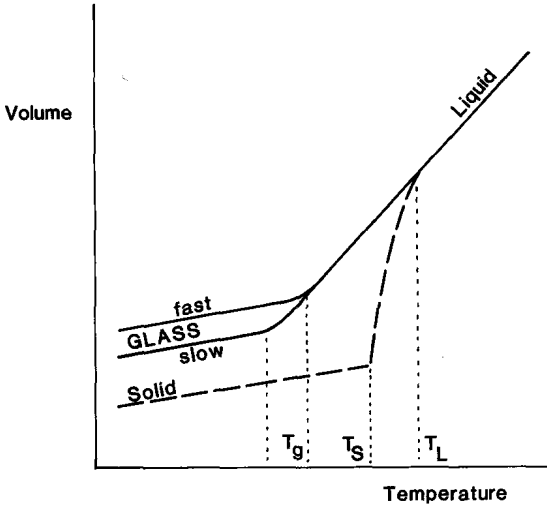
Figure 1.1   Schematic diagram of the change in volume on cooling of a typical multi-component glass melt showing the difference between a melt which comes to equilibrium by crystallizing and one that forms a glass; also how rate of cooling affects properties in and below the transformation range. Temperatures marked are: T_L the liquidus, T_S the solidus, and T_g the glass transition.

stresses, which is the usual purpose of annealing. It is sometimes useful to describe a glass as having a *fictive temperature*, meaning the temperature at which the existing structure would be the equilibrium one: from what has already been said about rates of relaxation, it will be evident that the fictive temperature must lie within the transformation range. If the material is truly glassy it can be cycled at will through the glass transition and a previous condition re-established: some apparently amorphous materials can undergo only one transformation (to the true solid state) when heat treated and should not be called glasses.

High-performance glasses are clearly ones which perform better than previously possible in some important respect, but glasses are used for so many different purposes that this can cover a very wide range of properties and processes, as the contents of this book are intended to make clear. Such developments imply that the properties of materials are much better understood than they used to be and that this knowledge can be used to good advantage.

1.2   Characteristic properties of glasses

The special properties of glasses are related to their liquid-like structures. Glasses thus are isotropic and lack internal grain boundaries or

structural elements lying in specific orientations. The common glasses have atomic structures with largely covalent bonds which make them able to transmit light, and the optical properties which result from these properties have long been amongst their most valued attributes.

The very rapid change of viscosity with temperature is one of the most characteristic and interesting features of glasses and is the key to most forming operations. The range of practical interest is unusually broad and covers more than fifteen decades (see Figure 1.2). At high temperatures, most silicate glass melts are much more viscous than other common materials but still flow easily under gravity or other relatively low stresses. They show Newtonian behaviour (rate of flow is proportional to shear stress, in isothermal conditions) and a rod, even one of varying diameter, is therefore easily drawn down to a much smaller diameter without necking and consequent fracture. When cooled sufficiently the glass becomes so viscous that it behaves like an elastic solid, but there is an intermediate region of *viscoelastic* behaviour in which both viscous flow and elastic deformation must be taken into account. Quantitative description of flow behaviour in this range is a complex task but an excellent discussion related to the tempering of glass is given by Gardon (1980). Rekhson (1984) gives a more general account.

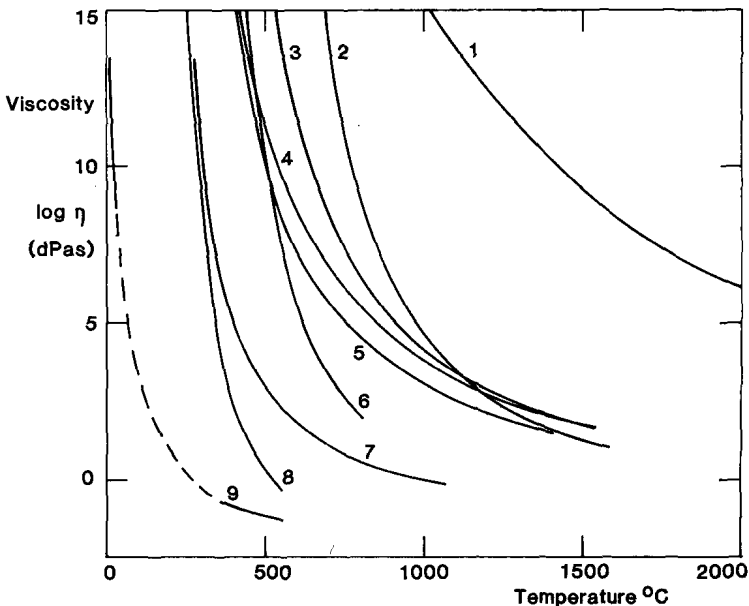**Figure 1.2** The viscosity–temperature characteristics of some important glass forming liquids: 1. pure silica; 2. a glass for fibre insulation; 3. a modern container glass; 4. English lead crystal; 5. sodium disilicate; 6. sodium diborate; 7. sodium metaphosphate; 8. a heavy metal fluoride glass; 9. a glassy metal (Au–Ge–Si).

Methods of glass forming thus depend on taking the melt at a temperature where gravity does not make flow too rapid, then simultaneously applying forces to shape it and cooling it to make it rigid as soon as the forming is finished. Simple shapes such as circular rods and tubes and spherical bulbs can be shaped without using moulds, but more complex items such as containers use moulds, the glass being made to flow by compressed air, pressing, or occasionally suction. The viscosity–temperature relation is crucially important to the technology of glass manufacture and is the first information a glass manufacturer would want to know if asked to produce a completely new kind of glass. Although the viscosity of typical silicate glasses varies greatly with temperature, the range of temperatures over which forming operations may be done is about 350 °C and almost any desired type of product can be formed by suitable control of temperatures and rates of cooling. The viscous properties of typical silicate glass melt have made hand forming, with or without moulds, a versatile method of production, which needs only very simple tools but much skill, and it has been exploited for several thousand years. Extensive mechanization of glass-forming operations has occurred only within the past century: the major processes have recently been reviewed by Cable (1991). Some high-performance glasses have even steeper viscosity–temperature curves than the common silicate glasses, and the very precise control of temperature which is then needed can be a source of considerable difficulty in glass-forming operations.

Apart from its importance to the glass technologist, the rapid change of viscosity with temperature gives an obvious and useful qualitative insight into why many viscous liquids can form glasses. Viscosity measures the ease with which ions or other small groups of atoms can rearrange themselves under the influence of stress, and a sufficiently high viscosity at the liquidus, where crystallization ought to occur, can mean that it is very difficult for crystals to form. The earliest fruitful picture of glass structures was the *random network hypothesis* of Zachariasen (1932), who considered the geometrical constraints required to build up extended but slightly irregular three-dimensional structures in which the bonding requirements of every atom were satisfied without appreciable distortion. This is an essentially static model which addresses the question of how a somewhat disordered material can have an energy content only a little greater than that of the true equilibrium crystalline form. Consideration of the structures of oxides led Zachariasen to suggest a set of rules which showed that only materials built up from tetrahedral or triangular units sharing corners but not edges or faces could be expected to form glasses. Slight variations in the angles of the bonds forming the hinges between adjoining units allow a long-range structure to avoid the exact regularity of a crystal. These rules gave, and

still give, valuable qualitative insight into many aspects of oxide glass behaviour but fail to include all glassy systems; most organic glasses do not have such structures, and nor does sulphur, which forms a glass if melted and cast into water.

Suppression of crystallization is the key to glass formation and must involve kinetics. Crystallization requires the rearrangement of ions or atoms to construct the crystal lattice and, even though the driving force and the details of the rearrangement are difficult, it is natural to link high viscosity with low atomic mobility (as in the classic Stokes–Einstein equation) and thus with very low rates of nucleation or growth of crystals. Typical silicate melts are so viscous, even at high temperatures, that it is easy to understand why crystallization can be suppressed by moderately rapid cooling and a glass easily formed. However, as Figure 1.2 shows, not all glasses are formed from highly viscous melts and other criteria are needed. The most useful approach is to use theories of rates of crystal nucleation and crystal growth to estimate the rate of cooling needed to prevent detectable crystallization. If a melt can be cooled more rapidly than this it should be possible to produce it in glassy form. The maximum rate of nucleation nearly always occurs at a temperature considerably lower than that at which crystal growth is most rapid (see Figure 1.3), so that crystallization, or *devitrification*, is more readily avoided during cooling than on subsequent reheating.

The maximum rate of cooling achievable in practice depends on both the size of the body being cooled and its thermal properties. For given
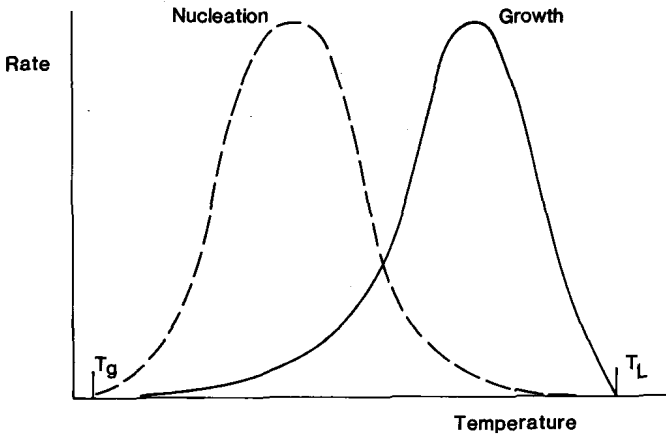
Figure 1.3 Schematic diagram of the temperature dependence of rates of crystal nucleation and crystal growth in typical glasses. Note that there is often a range just below the liquidus where, although growth is possible, nucleation is so slow that very few crystals are likely to form; such a melt can be held a little below the liquidus without devitrifying. Both nucleation and growth become extremely slow in the transformation range.

conditions at the surface, the rate of cooling inside a simple shape such as a flat slab or a cylinder is proportional to its thermal conductivity but inversely proportional to the square of its thickness or diameter, if these are the only two variables. Only products of small thickness or diameter can therefore be produced if rapid cooling is needed to form a glass. The most obvious example of this is the production of glassy metals, which has been reviewed by Vander Sande and Freed (1983). Here the necessary very high rates of cooling of the extremely fluid melts can only be achieved because the melts have high thermal conductivities and are formed into thin ribbons.

The ease with which a glass can be formed and worked may thus depend on several properties besides its viscosity–temperature relation and stability against crystallization; these include thermal conductivity, heat capacity, and transparency to thermal radiation. Theories of glass formation were discussed in detail by Rawson (1967) and a more recent good review is by Uhlmann and Yinnon (1983).

Because of the important uses of glassy thin films and fibres in electronics and optical communication systems, there is a very active current interest in pushing glass-forming capabilities to their limits. Various systems other than metals, which are difficult to produce as glasses, are being widely studied especially for optoelectronic devices. Amongst the most important of these are heavy-metal halide glasses (see chapter 13). Although the manufacture of these has its difficulties, many of them are much easier to produce than glassy metals; some halide glasses can be made up to 25 mm thick.

Once cooled, a glass has quite different properties. Although glasses are characteristically brittle and rather weak in practice, the poor strength is due to surface damage and not to the fundamental nature of the material. Pure silica, which has covalent bonds and should be very strong, is easily prepared without much loss of its theoretical strength and, unlike most other glasses, does not lose strength simply by being exposed to the air, because it has little susceptibility to corrosion by water vapour. Maintaining the high strength that ought to be possible with many glasses in an active field of endeavour. One obvious way to preserve their strength is to apply coatings which may prevent surface damage but, as Kirkbride and Williams show in chapter 4, there are many other advantages of applying surface coatings. Another method of improving strength is to convert the glass to a fine grained glass ceramic, and these materials are discussed by James and Jones in chapter 6. Many glasses are hard and working them in the solid state (cutting, grinding and polishing) requires methods entirely different from those used at high temperatures. In these conditions the isotropic nature of the material assists the production of a high-quality polish and the ability to hold very finely detailed structures.