

HIGH - PERFORMANCE
GLASSES

Edited by
M. Cable & J.M. Parker

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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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Contents

1 High-performance glasses	1
M. CABLE	
1.1 Introduction	1
1.2 Characteristic properties of glasses	2
1.3 Natural glasses	7
1.4 The evolution of man-made glasses	7
1.5 The development of glass technology	8
1.6 The relation between glass composition and properties	12
1.7 Glass melting	13
1.8 Modern applications of glasses	16
2 Glass formation from gels	20
I. STRAWBRIDGE and P. F. JAMES	
2.1 General introduction	20
2.2 Reaction chemistry of the sol-gel process	21
2.2.1 The alkoxide process	21
2.2.2 The aqueous route	22
2.2.3 Gelation in alkoxide systems	23
2.2.4 Gel ageing and drying	27
2.2.5 The gel-to-glass transition	29
2.2.6 Comparison with melted glasses	31
2.3 Applications	32
2.3.1 Coatings	32
2.3.2 Bulk glass samples	34
2.3.3 Glass fibres	38
2.3.4 Porous glass products, powders, spheres	41
2.3.5 Ceramics	44
2.3.6 Composites	45
2.3.7 Refractories	48
2.4 Conclusions	48
3 Oxynitride glasses	50
D. P. THOMPSON	
3.1 Introduction	50
3.2 Representation	51
3.3 Nitrogen incorporation	51
3.4 Characterization	53
3.5 Structure	54
3.6 Properties	56
3.7 Carbon-containing glasses	57
3.8 Nitrogen glass ceramics	58
3.9 Applications	60
4 Coatings on glass	63
B. J. KIRKBRIDE and G. WILLIAMS	
4.1 Introduction	63
4.2 Deposition methods	63

4.3	Improvement of strength and abrasion resistance	65
4.4	Coatings for optical systems	66
4.4.1	Thin-film optical design	66
4.4.2	Anti-reflection films	66
4.4.3	Mirrors	67
4.4.4	Edge filters	68
4.4.5	Band-pass filters	68
4.5	Architectural coatings	69
4.5.1	Off-line solar-control coatings	70
4.5.2	Off-line low-emissivity coatings	72
4.5.3	On-line architectural coatings	73
4.6	Automotive coatings	74
4.7	Transparent conducting coatings	76
4.7.1	Anti-reflection metal coatings	77
4.7.2	Transparent conducting oxides	77
4.8	Thin-film devices	80
4.8.1	Thin-film solar cells	81
4.8.2	Variable-transmission windows	82
4.8.3	Flat-panel displays	83
5	Glasses for flat-panel displays	86
	W. H. DUMBAUGH, P. L. BOCKO and F. P. FEHLNER	
5.1	Introduction	86
5.2	The role of sodium	88
5.3	Sheet-forming processes	89
5.4	Glass compositions	92
5.5	Rationale for flat-panel display substrate requirements	95
5.5.1	Dimensional precision	95
5.5.2	Thermal requirements	96
5.5.3	Chemical durability	98
5.5.4	Surface and bulk defects	99
5.6	Advanced technologies for flat-panel displays	100
6	Glass ceramics	102
	P. F. JAMES and R. W. JONES	
6.1	Introduction	102
6.2	The formation of glass ceramics	103
6.2.1	Heat-treatment schedule for glass-ceramic preparation	103
6.2.2	Crystal nucleation in glasses	104
6.2.3	Nucleation agents	113
6.3	Applications of glass ceramics	116
6.3.1	Introduction and general review	116
6.3.2	Glass-ceramic-metal substrates	118
6.3.3	Glass-ceramic matrices for composites	123
6.3.4	Glass-ceramic armour	127
6.3.5	Machineable phosphate-based glass ceramics	130
7	Electrical glasses: ionically conducting systems	133
	M. D. INGRAM	
7.1	Introduction	133
7.2	Conductivity-composition trends	134
7.3	Theoretical models for ionic conduction	137
7.3.1	The 'classical' model	137
7.3.2	The weak-electrolyte theory	138
7.3.3	Cluster-tissue models	139
7.4	Glassy electrolytes in advanced batteries	140

7.5	Anionic conductivity	141
7.6	The mixed mobile-ion effect	142
7.7	Dielectric properties	144
7.8	The glass electrode	145
7.9	The future	146
8	The bioactivity of glasses	148
	K. H. KARLSSON	
8.1	Introduction	148
8.2	Bone formation	149
8.3	Silicon in tissues	152
8.4	Bioactive glasses	153
8.5	Bioactive glass ceramics	158
8.6	Materials for prostheses	159
8.7	Glossary	160
9	Slow-release glasses	161
	P. KNOTT	
9.1	Introduction	161
9.1.1	Glass-ionomer cements	162
9.1.2	Glasses used in dental cements	162
9.1.3	$\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ glasses	163
9.1.4	$\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2$ glasses	167
9.1.5	$\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-CaF}_2$ glasses	169
9.1.6	Phase-separated glasses	170
9.1.7	Properties of glass-ionomer cements	172
9.1.8	Applications	174
9.1.9	Setting reactions	174
9.1.10	Future trends	175
9.2	Slow-release phosphate-glass systems	176
9.2.1	Dissolution mechanism	176
9.2.2	Controlled-release glasses	177
9.2.3	Trace-element deficiencies in ruminant animals	178
9.2.4	Effect of trace-element deficiencies	179
9.2.5	Treatment for deficiency	180
9.2.6	Use of soluble glasses to provide trace elements to animals	180
9.2.7	Glass compositions	181
9.2.8	Administration and operation	181
9.2.9	Other applications of soluble glasses to ruminant animals	183
9.2.10	Future trends	186
10	Controlling the durability of nuclear-waste glass	187
	M. J. PLODINEC	
10.1	Introduction	187
10.2	Objective of waste vitrification	188
10.3	Parameters affecting glass durability	188
10.4	Vitrification processes	189
10.4.1	Feed preparation	190
10.4.2	Glass melting	191
10.4.3	Glass pouring	192
10.5	Glass formulation	193
10.5.1	Constraints	193
10.5.2	Composition development	194
10.5.3	Optimization criteria and process	194
10.5.4	Result	195

10.6	Control of glass composition for durability	197
10.6.1	Requirements for a tool to assess glass composition	197
10.6.2	Selection of the tool	198
10.6.3	Free energy of hydration approach	198
10.6.4	Use of free energy for control	203
10.7	Glass performance in the repository	206
10.7.1	Laboratory repository-simulation tests	206
10.7.2	<i>In situ</i> testing	207
10.7.3	Modelling	207
10.8	The future	208
10.9	Conclusions	208
11	Optically non-linear glasses	210
	B. J. AINSLIE	
11.1	Introduction	210
11.2	Origin of non-linearity	212
11.3	Highly non-linear glasses	216
11.4	Semiconductor-doped glasses	220
11.5	Waveguides and device structures	221
11.5.1	Non-resonant glasses	221
11.5.2	Semiconductor-doped glass waveguides,	225
11.6	Future prospects	228
12	Advanced optical components	229
	L. ROSS	
12.1	Fundamentals of gradient-index glasses	229
12.2	Methods of producing refractive-index gradients in glasses	230
12.2.1	Ion exchange in glasses	230
12.2.2	Ion stuffing in leached glasses	235
12.2.3	Chemical vapour deposition	236
12.2.4	Ion implantation	238
12.2.5	Fused layers	238
12.2.6	Sol-gel process	239
12.3	Optical elements based on GRIN structures	240
12.3.1	GRIN lenses for classical optical applications	241
12.3.2	Integrated optical devices in glass	243
12.3.3	Fibre optics for light and data transmission	247
12.4	Summary and conclusions	251
13	Infrared-transmitting optical fibres	252
	J. M. PARKER and A. B. SEDDON	
13.1	Introduction	252
13.1.1	Optical properties of fibres	252
13.1.2	The development of silica-based glass fibres	257
13.1.3	Infrared-transmitting fibres	259
13.2	Oxide-based systems	262
13.3	Chalcogenide and chalcohalide glasses	263
13.3.1	Compositions	263
13.3.2	Fabrication	264
13.3.3	Optical characteristics of glasses	268
13.3.4	Mechanical and chemical properties	271
13.4	Halide glasses	272
13.4.1	Compositions	272
13.4.2	Fabrication	276
13.4.3	Optical properties	278

13.4.4	Mechanical and chemical properties	279
13.4.5	Further developments	280
13.5	Hollow-core fibres	280
13.5.1	Compositions	280
13.5.2	Fabrication	281
13.5.3	Optical properties	281
13.6	Applications	284
14	Photo-induced changes in chalcogenide glasses and their applications	287
	P. J. S. EWEN and A. E. OWEN	
14.1	Introduction	287
14.2	The classification of photo-induced effects in chalcogenide glasses	288
14.3	Reversible photo-induced effects	289
14.3.1	Photo-induced changes in local atomic structure	289
14.3.2	Photodecomposition	291
14.4	Irreversible photo-induced effects	293
14.4.1	Photocrystallization	293
14.4.2	Photopolymerization	293
14.4.3	Photo-induced morphological changes	294
14.4.4	Photovaporization	294
14.4.5	Photodissolution of metals	295
14.5	Applications of light-induced effects in chalcogenide glasses	298
14.5.1	Imaging properties of the photodissolution effect	298
14.5.2	VLSI lithography	298
14.5.3	Infrared diffractive effects	303
14.5.4	Optical mass memories	306
14.5.5	Integrated optics	307
14.6	Conclusions	308
	References	310
	Index	339

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

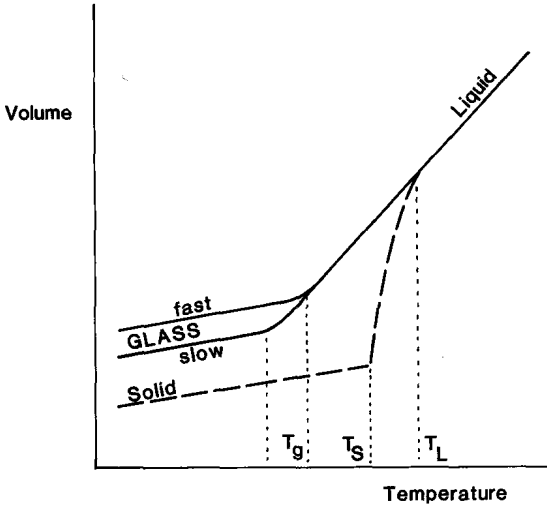


Figure 1.1 Schematic diagram of the change in volume on cooling of a typical multi-component glass melt showing the difference between a melt which comes to equilibrium by crystallizing and one that forms a glass; also how rate of cooling affects properties in and below the transformation range. Temperatures 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.

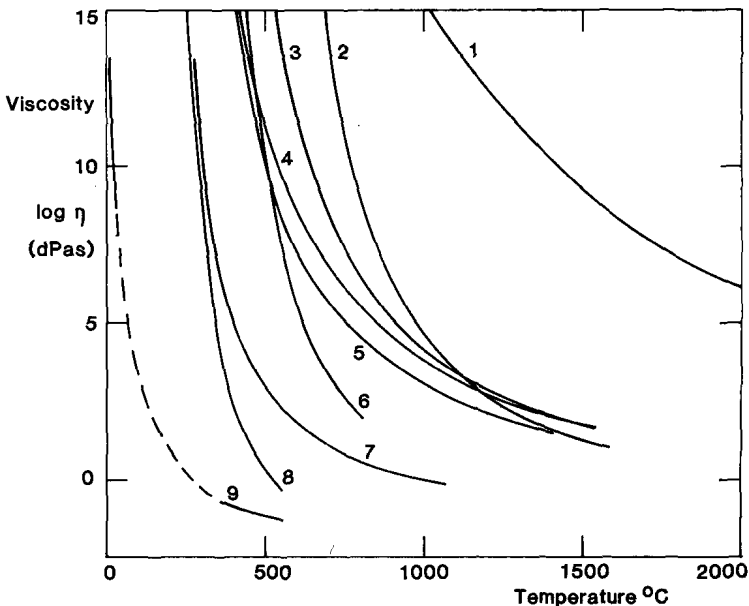


Figure 1.2 The viscosity-temperature characteristics of some important glass forming liquids: 1. pure silica; 2. a glass for fibre insulation; 3. a modern container glass; 4. English lead crystal; 5. sodium disilicate; 6. sodium diborate; 7. sodium metaphosphate; 8. a heavy metal fluoride glass; 9. a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

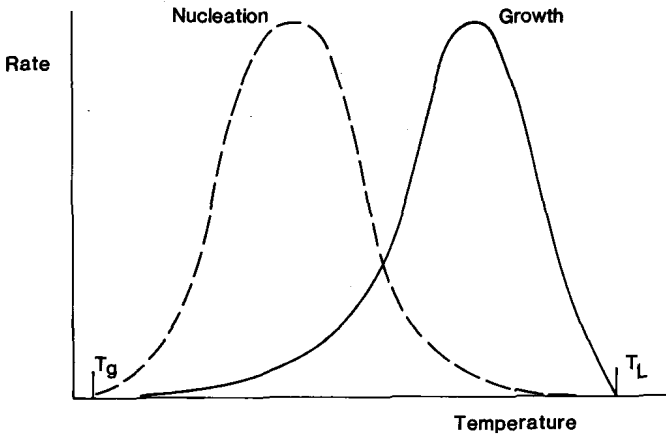


Figure 1.3 Schematic diagram of the temperature dependence of rates of crystal nucleation and crystal growth in typical glasses. Note that there is often a range just below the liquidus where, although growth is possible, nucleation is so slow that very few crystals are likely to form; such a melt can 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.