

Encyclopedia of Glass Science, Technology, History, and Culture

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Abstracts of chapters

Section I. Glassmaking	3
Section II. Structure	8
Section III. Physical properties	14
Section IV. Transport properties	23
Section V. Chemical properties	27
Section VI. Glass and light	35
Section VII. Inorganic glass families	41
Section VIII. Organically related glasses	48
Section IX. Environmental and other issues	54
Section X. History of glass	61

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General introduction

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Already in prehistory the fundamental importance of glass was simply demonstrated by the fact that its unique cutting properties made obsidian one of the first substances extensively traded over long distances. Likewise, man-made glass probably represented the first case of a global market when ingots and finished products made in the Eastern Mediterranean were exported throughout the Ancient world at the beginning of our era. Glass has long been the preserve of silicates. Interestingly, the silica sand used as a starting material results from a quantum-chemical effect at work in the geological process termed magma differentiation. As for the flint originally used to make *flint glass* in the 17th century, its source is amorphous silica biologically produced over long periods of time. Since then, the chemical compositions, production processes and uses of the material have so much diversified that one can claim that we are now living in the Glass Age. Whether organic or inorganic, a glass follows the same phenomenology. When cooled from the liquid state, it loses internal thermodynamic equilibrium. It becomes a metastable material in a temperature interval, the glass transition range, which shifts to higher temperatures with shorter observation timescales and higher cooling rates. At a microscopic scale, this transition represents the irreversible freezing in of the atomic structure and the loss of the so-called configurational degrees of freedom. As a result, the associated contributions to second-order thermodynamic properties (heat capacity, thermal expansivity and compressibility) are also lost so that properties of the glass formed such as enthalpy, entropy or volume depend on the particular conditions of the experiment. Relaxation then is a fundamental feature since it describes the kinetics at which equilibrium is lost upon cooling or regained upon heating. As a first step, it can be dealt in terms of Maxwell model of a spring and dashpot placed in series whose parameters depend on glass composition. Known as Kauzmann paradox, a simple argument points to configurational entropy as the driving force of the process and of its faster or slower kinetics exhibited by *strong* or *fragile* liquids extensively discussed in following chapters.

Section I. Glassmaking

1.1. Glass production: an overview

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In this chapter the variety of inorganic and organic glass-forming systems are first reviewed briefly. The focus is then turned to industrially manufactured glasses. The properties by which they stand out against other competitive materials are highlighted. An overview over the large number of different glass products and glass producing branches is given. The role of glass composition and its relevance to the glass-making process and to the resulting glass properties are successively treated in detail. Viscosity, liquidus temperature, and the tendency to undergo liquid unmixing are depicted as examples of the first category, elastic properties, thermal expansion coefficient, and chemical durability of the second. Finally, a few challenges regarding glass synthesis are addressed.

1.2. Raw materials for glass making: Properties and constraints

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Batch specifications may in principle be respected in a great many different ways as indicated by a comprehensive summary of the raw materials currently available. In glass making, however, both quality and throughput critically depend on the size distribution and impurity content of the raw materials used because the complex melting process must be kept as short as possible to optimize production costs. When not properly managed, raw materials result in optical defects or chemical and physical heterogeneities that can even cause manufacturing to stop. To guarantee high-quality glass production, the appropriate procedures for handling raw materials thus consist of quantifying refractory minerals such as chromite and corundum by heavy-mineral separation techniques, and of determining moisture, particle-size distribution, loss-on-ignition, apparent density, chemical oxygen demand, and bulk chemistry. Contaminants, such as ceramics, glass ceramics, aluminium metal or Ni-bearing materials are

all detrimental to the glass-making process and thus proscribed in glass-maker specifications. In instances such as solar-energy applications, extra-clear glasses are needed with the additional constraint of iron-contents lower than 100 ppm.

1.3. Fusion of glass

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By building a bridge between technological and scientific aspects of glass making, this chapter describes glass fusion from a batch of granular, solid raw materials until the establishment of a thermally and chemically homogeneous melt. After a bird's eye presentation of the technology of industrial glass fusion, the thermochemistry and kinetics of the distinct steps are treated in detail, one by one, along the process road. With the help of real examples, this approach comprises the preparation of a raw material batch – with a special focus given to batch calculation resting on the results of raw materials analysis – primary melting reactions, the ultimate dissolution of residual solids, and the clearance of the melt from gas bubbles. A quantitative approach to the energy demand of glass fusion is given. Finally, a few areas of future development are highlighted.

1.4. Primary fabrication of flat glass

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From the beginning of the 20th century flat glass has been produced directly by various processes to by-pass the first step of glass blowing that was until then needed to yield transparent sheets with a fire polish. In various ways, meter-wide glass ribbon was drawn upward and then annealed in processes that were continuous during more or less limited periods of time. Since the middle of the 20th century one has obtained flat sheets with fire polish on both sides by pouring the molten glass onto a bath of molten tin under a slightly

reduced atmosphere. This *float* process established by Pilkington Brothers was a real industrial revolution because the truly continuous nature of its operation yielded at a reduced cost glass sheets with a width of up to over 3 m and thicknesses now ranging down to less than 0.4 mm and up to around 25 mm. Even though worldwide flat glass production has experienced a 90-fold increase since its introduction, this process is coexisting with others that are either more versatile or better suited for specific applications or glass compositions. The traditional *roll out* process is for example still used to produce patterned and wire-reinforced glass whereas the *fusion downdraw* process is suited to specialty glass, for instance for display substrates and chemically strengthened products, as well as for a variety of ultra-thin products. However research is pursued to improve current processes and to satisfy market demands for new applications through original functionalities.

1.5. Fabrication of glass containers

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The making of glass-container is one of the most complex in the glass industry in which critical interactions are thermal during the highly non-isothermal forming process and possibly mechanical between glass and molds during forming. Depending on the way in which the initial glass gob is turned into a parison that is then shaped, three different processes are distinguished, namely, Blow & blow, Press & blow and Narrow-neck press & blow whose principles are expounded and their applications described. For this purpose, an overview of actual forming machines is given, the complex relations between glass-properties and machine-actions is explained, and the systematic quality control performed is described. Importantly, the complexity of the process is adequately dealt with a high automation level that is hardly recognized in the final product, but is necessary to ensure the high economic efficiency of the process as well as high standardization and competitiveness of the product.

1.6. Continuous glass fibers for reinforcement

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An overview of the development of glass fiber technology for commercial use in reinforced composite applications is presented. We thus describe a broad spectrum of glass fiber technology, beginning with the early technology of E-glass fibers, still the predominant form of glass fibers in use today for reinforcements, and moving forward to the leading glass fiber developments driving new market applications. The evolution from fibers made by spinning of conventional soda-lime glasses into insulation fibers to an array of commercial reinforcing fiber compositions is discussed. The E-glass fiber compositions, which primarily lie within the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ system and were developed for their excellent electrical properties, are then examined, along with the accompanying suite of strength, stiffness, and light weight properties that ignited the growth of the GRP composites industry. Changes in glass composition to drive specific attributes such as strength, modulus, dielectric constant, and acid corrosion resistance are reviewed, illustrating the developments of high performance fibers. Surface chemistry elements, manufacturing process considerations, and product attributes are discussed. Market applications with breakdown by regions globally and major fiber glass producers at present are finally summarized.

1.7. Simulation in glass processes

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The purpose, process, and foundation of numerical simulations applied to glass processes are described, with special attention to fluid dynamics and heat transfer. Important transport phenomena are discussed and presented as partial differential equations in a common form known as the advection-diffusion equation, along with the radiative transfer equation to account for energy transfer by emission, absorption, and scattering of IR radiation in semi-transparent media. The manner in which these transport equations are coupled to each other, as well as their interactions across interfaces within a process, are described; and common

post-processing techniques, which provide insights and/or performance indices, are reviewed. Simulation examples of phenomena in glass melting furnaces, conditioning, and forming processes are discussed. Also, the value of implementing a system to manage simulation data is discussed.

Section II. Structure

2.1. Basic concepts of network glass structure

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As a solid material with a non-crystalline structure, a glass has short-range order, but not long-range order. Hence there is no unit cell to form the basis of a description of its structure. For oxide and chalcogenide glasses, the dominant structural model remains the random network defined by Zachariasen's celebrated rules. With reference to that of SiO_2 , the usual archetype, the structure of oxide network glasses is described on the basis of $\text{SiO}_{4/2}$ tetrahedra, which are very well defined, and of their random arrangement that arises from the distribution of bond and torsion angles between pairs of connected tetrahedra. After the difficulties met by micro-crystalline models of glass structure have been briefly explained, the structural role of modifiers, such as Na_2O , is described. The addition of modifier to a glass leads to either the breaking of oxygen bridges or to an increase in the average glass-former coordination number. Intermediate-range order, for example the occurrence of rings, is then discussed briefly. Finally, the structure of chalcogenide glasses is presented, and their differences from that of oxide glasses pointed out.

2.2. Structural probes of glass

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In this chapter several of the common methods for probing the structure of glasses are briefly discussed beginning with the direct structural probes, X-ray and neutron diffraction, that give information on the averaged bulk structure. With these techniques one can obtain information on bond distances and angles and determine a broad overview of the general nature of the glass network. Other X-ray techniques such as X-ray absorption spectroscopy (XAS) are used for probing atom-specific and more localized structure such as coordination numbers, bond distances, oxidation states and electronic structure. Nuclear magnetic resonance (NMR)

spectroscopy can further determine the nature of the oxygen environment, proportion of bridging (BO) and non-bridging oxygens (NBO), types of bridging oxygen linkages, as well as types and numbers of Q species (tetrahedra with 1-4 BOs), and coordination of appropriate cations such as aluminum (Al), silicon (Si) and boron (B). Raman spectroscopy is a vibrational spectroscopy technique that uses the vibrations of the oxygen atoms and network modifiers to discriminate both short-range structures (Q species) and intermediate-range structures (rings) within glass networks. Brillouin spectroscopy measures the elastic behaviour of glasses and is used to define polyamorphic phase transitions. Finally, several more specialized techniques are introduced including Mossbauer spectroscopy for determining Fe and Sn oxidation and coordination states, X-ray photoelectron spectroscopy (XPS) for determining proportions of NBO, BO and free oxygen, Ultra violet/Visible spectroscopy (UV/Vis) for determining the nature of the transition metals that cause colour in glasses, and finally Infra-Red (IR) spectroscopy for probing the structure of borate and borosilicate glasses.

2.3. Microstructure Analysis of Glasses and Glass Ceramics

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This chapter describes the most informative methods to image and analyze the micro- and nanostructure of inhomogeneous glasses and glass ceramics and relate these features to their original physical or chemical properties. For imaging, the main methods are scanning and transmission electron microscopy. In combination with them, energy-dispersive X-ray spectroscopy and electron-energy loss spectroscopy can be used to determine chemical compositions and to elucidate coordination states and valences, respectively, with a spatial resolution in the nm range. Also depicted briefly are other techniques available for image-formation of the micro- and nanostructure, such as atomic force microscopy and advanced X-ray microscopy. For all of them the instrumental constraints are specified along with their advantages and drawbacks as illustrated with a common magnesium aluminosilicate glass ceramics.

2.4. Short-range structure and order in oxide glasses

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Data from spectroscopy and studies of X-ray and neutron scattering show considerable short-range order in oxide glasses, most well defined in the first shell coordinations of network forming cations. Many other aspects of structure also show signs of non-random ordering when quenched in at the glass transition temperature, and can be sources of increased disorder at higher temperatures. How structural groups link together, how bridging and non-bridging oxygens are distributed through the network, how cations and anions mix among different bonding environments, and what coordination numbers are present all can be measured in at least some simple systems, and are known to change greatly with composition, temperature and pressure. Making detailed connections between glass structure and properties often remains difficult. New experimental technologies, and advanced theoretical methods that can more quantitatively link models to data, continually lead to progress with this ongoing challenge.

2.5. The extended structure of glass

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Glasses are monolithic materials and their extended structure ranges from the physics and chemistry played out on the atomic and nano-scale, to the engineering dimensions of cast products. Very few defects are generated during glass solidification, apart from microcracks at the surface, making glassy materials and their extended structures uniquely different from crystalline materials. This account draws together experimental techniques that probe on many length scales the structures of insulating network glasses, as well as those of metallic glasses. The extended structure has common elements for non-conducting as well as conducting glasses. It ranges from average static atomic nearest neighbour arrangements, correlations between free volume voids, to many-atom structural dynamics and density fluctuations. The latter are signatures of the non-ergodicity of the supercooled state captured

close to the glass transition. As individual experimental techniques necessarily underdetermine glass structure, computational modelling is essential to assemble three dimensional structures that agree with different independent experiments. This is particularly important in studying complex glasses which are invariably not homogeneous, even on the atomic scale. Indeed, clarifying this heterogeneity helps to throw light on the different applications of glasses. In bringing together observation and modelling of glass structures, the main aim of this chapter is to visualise their extended nature, starting on the scale of atoms and molecules, in order to try and understand functionality on the macro scale.

2.6. Structure of chemically complex silicate systems

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The structure and structure-property relationships of chemically complex glass and melts are treated in terms of the behavior of unary to quaternary silicate and aluminosilicate systems. It is assumed that the principles and structural concepts from such experimental studies are directly applicable to more complex systems including natural magma and commercial glass compositions. The simplest silicate glass is SiO_2 . Its short- and mid-range structure resembles that of its liquidus phase, cristobalite. Substitution of Al^{3+} for Si^{4+} to form aluminosilicate tetrahedra results in gradual structural changes of the SiO_2 structure. Phosphorus, Ti^{4+} , and Fe^{3+} may also be tetrahedrally coordinated, but if so, likely form tetrahedral complexes distinct from the aluminosilicate network. These cations may also form clusters in the structure. Addition of alkali metals, which induces formation of nonbridging oxygen and coexisting Q^n -species, causes Al^{3+} to substitute for Si^{4+} primarily in the most polymerized of the Q^n sites. In chemically complex melts resembling natural magma, alkali metals are the principal charge-balancing cation for tetrahedrally-coordinated Al^{3+} , whereas alkaline earths (Ca^{2+} and Mg^{2+}) are dominant network modifiers. These simple structural relationships are valuable to interpret the physical and chemical properties of such glasses and melts.

2.7. Topological constraint theory of inorganic glasses

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Originally, the topological constraint theory (TCT) represented simple theoretical inquiries about the existence of Zachariasen's topologically disordered networks and easy glass formation. Over the last 25 years it has evolved to a widely used formalism for modeling composition-property relationships in glasses and glass-forming liquids. Although somewhat approximate and lacking fundamental basis, TCT yields results that are in good agreement with observations. This is largely because it takes as input experimentally (or model-based) information on the variation of structure with composition and a theoretically sound temperature dependence of chemical-bond strengths. In this chapter, we review the basic concepts and the recent extension of TCT to temperature-dependent bond constraints. In addition, some of the fundamental issues that remain unresolved are highlighted.

2.8. Atomistic simulations of glass structure and properties

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In numerical simulations of glass structure and properties the atomic coordinates of a large set of atoms making up a glass or melt system can be evaluated theoretically under a variety of physical conditions once an appropriate model has been designed to account for their mutual interactions. The most popular methods are Monte-Carlo and molecular dynamics simulations. The former is less time consuming because it probes only the region of the phase space that contributes the most to the partition function but is restricted to equilibrium states. The latter is much more demanding computationally as at every moment it solves the equations of motion for all the atoms of the system, but it has the advantage of providing a complete dynamical description of the system regardless on the equilibrium or non-equilibrium nature of the states investigated. In contrast to experimental probes that mainly give insights on short-range order, atomistic simulations provide information not only on short-but also on medium-range structures. An additional advantage of atomistic simulations

is that they can readily yield structural and physical information for any system for which experimental data are completely lacking.

2.9. First-principles simulations of glass-formers

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In this chapter we review results of computer simulation of glasses carried out using first principles approaches, notably density functional theory. We first compare this approach with the one of simulations with classical potentials and then discuss how it helps to get insight into the properties of simple and complex glasses. For this purpose, we focus on the radial distribution functions, the structure factor, the vibrational densities of states, as well as NMR spectra. In all these cases, *ab initio* simulations prove to be useful to get a good understanding of the properties of glasses on the microscopic level.

Section III. Physical properties

3.1. Glass formation

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The glassy state of matter is briefly analysed with an emphasis on long-term stability and impediment of relaxation to a thermodynamically stable crystalline structure. Melt quenching as the basic method of glass formation is discussed and the kinetic conditions for vitrification described. Structural, microscopic and energetic criteria for glass formation are considered the notions of glass formers, intermediate and modifiers being explained. The glass transition is briefly analysed from the view point of topological rearrangements of the bonding system that lead to different properties of glasses and melts. The cooling-rate dependence of glass transition temperature is also discussed.

3.2. Thermodynamics of Glasses

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The thermodynamics of glasses and of the glass transition is reviewed phenomenologically. In view of its irreversible, kinetic nature, this transition cannot be described by equilibrium thermodynamics. The basic nonequilibrium concepts of order parameter and affinity are thus introduced to describe it and the properties of glasses, which cannot be represented in terms of only two state variables such as temperature and pressure. Calorimetric measurements on PVAc are in particular used to determine configurational heat capacities, enthalpies and entropies and their variations when internal equilibrium is lost in the glass transition range. These variations can be accounted for with relaxation models, which can in addition clearly distinguish the entropy irreversibly produced at the glass transition from the variations of the configurational entropy of the glass-forming liquid.

3.3. The Glass Transition and the entropy crisis

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Conventional theories to study glasses require considering a rapid drop in either the excess entropy ΔS_{ex} or the free volume V_f . The viscosity diverges when they vanish but at different temperatures, which casts doubt on the physical significance of the divergence in terms of the hypothetical ideal glass, which is supposed to be at its root. To elucidate the nature of the ideal glass, a recently developed nonequilibrium thermodynamics is instead used to determine how the entropy relaxes. If ΔS_{ex} is replaced by the communal entropy S_{comm} (not to be confused with the configurational entropy) and V_f is properly identified, the two quantities then vanish simultaneously in the ideal glass so that the latter is a jammed state with no free volume and communal entropy. Because the entropy of the supercooled liquid shows no mathematical singularities at the ideal glass transition, the two approaches become unified and the viscosity divergence uniquely specifies the ideal glass.

3.4. Atomic vibrations in glasses

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In glasses, atomic disorder combined with atomic connectivity makes understanding of the nature of the vibrations much more complex than in crystals or molecules. With a simple model, however, it is possible to show how disorder generates quasi-local modes on optic branches as well as on acoustic branches at low-frequency. The latter modes, possibly hybridizing with low-lying optic modes in real glasses, lead to the excess, low-frequency excitations known as “boson-peak modes”, which are lacking in crystals. The spatially quasi-localized vibrations also explain anomalies in thermal conductivity and the end of the acoustic branches, two other specific features of glasses. Together with the quasi-localization of the modes at the nanometric scale, structural disorder lifts the crystalline or molecular spectroscopic selection rules and makes interpretation of experiments difficult. Nevertheless,

vibrations in simple glasses such as vitreous silica or vitreous boron oxide are nowadays rather well described. But a comprehensive understanding of the boson peak modes remains a highly debated issue as illustrated by three archetypal glass systems, vitreous SiO_2 and B_2O_3 and amorphous silicon.

3.5. Density of amorphous oxides

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This chapter explores the importance of the density of amorphous oxides for a range of applications, from glass making to the Earth and planetary sciences. After introducing its general importance, the theoretical factors affecting density are presented. The principal experimental methods for measuring the density of solid and liquid amorphous materials in different temperature and pressure ranges are then presented. Once it is appreciated how and with what precision melt density can be quantified in the laboratory, the effects of temperature, pressure and composition are considered in more detail. Thanks to the large experimental database that it is available, empirical predictive models and the links between density and glass/melt structure are illustrated. Some practical applications of a detailed knowledge of melt density are presented, before finishing with some promising lines of future work that may lead to an even better understanding of this critical parameter.

3.6. Thermodynamic properties of oxide glasses and liquids

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The thermodynamic properties of glasses and liquids are reviewed from the vicinity of 0 K to nearly 2000 K. Below 200 K the low-temperature heat capacity and vibrational entropy of

silicate glasses are sensitive probes of short-range order and, thus, of oxygen coordination polyhedra for both network-forming and modifying cations such that the speciation of aluminum, boron and alkali cations must be taken into account. At the lowest temperatures the calorimetric boson peak is the most intense for glasses with high low field-strength modifying cations and often with high SiO₂ contents. Between room temperature and the glass transition, the composition dependence of vibrational properties tends to vanish. In the stable liquid, in contrast, the configurational heat capacity varies much with composition in a way reminiscent of the dependence of low-temperature properties. Models of calculations of these properties are presented, along with determinations of residual entropies from rheological measurements and calculations of Gibbs free energies of formations of glasses and liquids.

3.7. Structural, shear and stress relaxation in glass-forming liquids

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This chapter discusses thermo-viscoelasticity as it applies to the response of glass to thermal and mechanical loads in the temperature range of the glass transition. The impact of temperature history on the structure and on macroscopic properties is described by fictive temperatures the dynamics of which is calculated by the Tool-Narayanaswamy-Moynihan(-Mazurin-Rekhson-Startsev)-model. It is shown how the model parameters are determined from Differential Scanning Calorimetry. The simulations of thermal shrinkage and the cooling rate dependence of the refractive index demonstrate the predictive power of the model. As for the response to mechanical loads, common viscoelastic phenomena (elasticity, delayed elasticity, creep, stress relaxation) as well as material models (Maxwell, Kelvin-Voigt, Burger) are presented. The cases of volume-preserving shear and shape-preserving compression (or dilatation) are considered. For small strains, both are handled in a similar way. For large dilatational strain, however, the impact on glass properties and dynamics is taken into account by fictive pressures.

3.8. Hyperquenched glasses: Relaxation and properties

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This chapter describes the relaxation phenomena and physical properties of hyperquenched glasses (HQGs), *i.e.*, glasses far from equilibrium. A hyperquenching-annealing-calorimetry (HAC) approach is introduced for determining their fictive temperature and cooling rate. Specifically, it is used to explore enthalpy relaxation, thermal histories, and energetic and structural heterogeneities and, thus, the glass transition in general. This chapter demonstrates significant differences in enthalpy relaxation between strong and fragile HQ glasses and describes their intrinsic origin in terms of glass structure and potential-energy landscape. The impact of both hyperquenching and annealing on the vibrational and mechanical properties of HQ glasses is discussed. Finally, the HAC approach is an effective method for identifying various relaxation modes and for revealing the thermodynamic and structural origin of the fragile-to-strong liquid transition.

3.9. Polyamorphism and liquid-liquid phase transitions

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Polyamorphism is defined by the existence of different amorphous states of a given substance, with different structures and properties, between which transformations resembling crystalline phase transitions can occur. To describe this phenomenon we take as a starting point the first-order phase transitions (LLPT) that appear in liquids as a function of pressure and temperature and are driven by density or entropy contrasts between low- (LDL) and high-density (HDL) liquid phases. The HDL-LDL transitions can be extended below the glass transformation range to interpret polyamorphic transformations between LDA and HDA solid amorphous states. Polyamorphism can also reflect different relative population of minima within the

configurational energy landscape (CEL), or relaxation processes and changes within the CEL accessed by different synthesis and annealing protocols. We review the background to these effects with reference to classic systems that reveal different aspects of the phenomenology. Polyamorphism and LLPT represent an intrinsic part of the physical chemistry of liquids and amorphous solids and lead to opportunities for developing nanomaterials with hierarchical structures at different length scales.

3.10. Pressure-induced amorphization

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Pressure-induced amorphization (PIA) occurs as a crystalline solid is compressed beyond its normal stability range at a temperature too low or on a rapid timescale so that expected crystalline phase transformations can not be initiated or completed. The superpressed crystal may encounter an intrinsic elastic or mechanical stability limit or may develop a critical concentration of defects so that it transforms into an amorphous version of the same substance. Amorphization can also occur as high-density crystals prepared under high-pressure conditions are decompressed or heated metastably at low pressure. The solids produced by PIA can resemble high-density amorphous (HDA) phases that transform into more conventional low-density (LDA) forms upon decompression. The PIA event can be described as analogous to a metastable melting event occurring below the glass transformation range or as mechanical collapse of the crystal as its elastic stability limits are exceeded. PIA can also be described in terms of configurational energy landscape (CEL) models as the starting crystalline phase becomes destabilized. The process can result in new amorphous forms and amorphous-crystalline nanocomposites with high strength properties and other possible technological applications.

3.11. Mechanical properties of inorganic glasses

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Many glasses may be viewed as archetypal brittle materials being brittle, stiff and hard. Elastic moduli are related to the relatively high bond strengths in glasses but are also a function of the atomic packing densities. The relatively high bond strengths mean that atomic rearrangement under stress is difficult. Glasses thus have low fracture toughness values and are flaw sensitive, with surface flaws usually being dominant. As a result glass strength depends on component history and strength data have to be treated statistically. If glasses can be maintained in an essentially flaw-free state (as is the case of silica-fibre optics) then strengths approaching the theoretical value, obtained from a consideration of the bond strength, are achieved. Strength degradation of glasses with time arises from contact damage during use and, in the case of silicates, from subcritical crack growth due to scission of strained crack tip bonds by atmospheric water. Increased strengths can be achieved through the use of compressive surface residual stresses (thermally and chemically tempered glasses) or by flaw filling coatings that are well bonded to the glass surface.

3.12. Strengthening of oxide glasses

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The ways to strengthen oxide glasses are closely linked with surface defects, which act as stress amplifiers and thus reduce the practical strength of the material. In this chapter a concise summary as to how to measure strength and stress limits are discussed in terms of advantages and drawbacks of the various methods. Furthermore, an overview is provided of the different ways to eliminate previously formed surface defects, including the different types of polishing and etching. Avoidance of surface defect formation is also discussed in

terms of protective coatings as well as processing issues in the glass industry, such as cutting and finishing of glass products. Improvement of glass strength by inducing residual surface compressive stresses through thermal strengthening and different kinds of chemical strengthening is described. Finally, some applications through strengthening of oxide glasses and perspectives of the near future of thermal and chemical strengthening are provided.

3.13. Radiation effects in glass

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This chapter addresses the evolution of the structure and properties of glasses upon irradiation. Formation of point defects is first reviewed, mainly in silica glasses, along with bubble formation, phase separation and medium-range order reorganization. The evolution of optical and mechanical properties of the glass under radiation are then discussed with reference to radiation-induced attenuation in optical fibers and to rare earth-doped glasses. Current solutions used to limit radiation effects in glasses are finally described.

3.14. Amorphous ices

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Vitrification is observed under pressure at $T = T_{sg}$ from supercooled water. It is described in terms of enthalpy changes resulting from a competition between two liquids. In each, an additional enthalpy term is included in the Gibbs free energy of formation of superclusters at temperatures at which homogenous nucleation gives rise to ordered liquids upon supercooling. At the glass transition temperature $T_g \cong 136.2$ K the two ordered liquids coexist

when their enthalpy difference vanishes. A low-density amorphous phase of supercooled Phase 3 and an ordered liquid Phase 3 form at T_g . A first-order transition occurs at T_{sg} for $0.31 < P < 0.55$ GPa and yields a high-density amorphous Phase 3 whose T_g is $0.65 T_m$. The ordered liquid Phase 3 superheats at a temperature higher than the melting temperature T_m and gives rise to a very high-density phase at $P \cong 0.95$ GPa. A liquid-to-liquid transition exists at $T_{LL} \cong 0.84335 T_m$ for $-0.149 < P < 0.176$ GPa. Application of this phenomenology to other glass-forming liquids is also discussed.

Section IV. Transport properties

4.1. Viscosity of glass-forming melts

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This chapter shows the fundamental importance of viscosity to describe the fluid character of the synthetic and natural glass-forming melts relevant to industry and geosciences. The melt response to shear and normal stresses is in most cases defined by a constant ratio between stress and deformation rate. Only under extreme forming conditions and for heterogenic melts deviations from such a Newtonian viscosity are observed. On the atomistic scale, viscous flow is linked to the complexity of cooperative rearrangements of structural entities leading to a non-Arrhenian temperature dependence above T_g . In the glass transition range, viscosity becomes time-dependent as the timescale of structural relaxation exceeds those of the deformation process. The increasing inequality leads to the isostructural viscosity of the unrelaxed melt state at temperatures far below T_g . The various methods used to measure it over 14 orders of magnitude are described along with three-parameter equations used in practice to predict the viscosity-temperature dependence with high accuracy. Owing to their technical importance the effect of oxide components on viscosity is discussed especially in relation to changes in the connectivity of rearranging structural units, which are most prominently seen by the viscosity hump of the boron anomaly. Whereas viscous flow is generally governed by the fractions of major components, trace amounts of water have an exclusive role in accelerating the network dynamics. In addition, viscosity is strongly effected by microstructure, when inclusions are present in the melt. In case of crystal-bearing melts a strong increase in viscosity with increasing crystal fraction becomes evident, while bubbles tend to decrease viscosity if sheared at high capillary numbers.

4.2. Ionic and electronic transport

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As has been known for over a century, ionic transport in oxide glasses and melts is highly sensitive to temperature and chemical composition. These two factors are accounted for by classical models of ionic transport in ionic crystals and molten salts and electrolytic solutions thermodynamics, respectively. Of more recent interest, electronic conductive glasses are understood with theoretical approaches derived from well-established concepts of solid-state physics. The transfer of electrons from one localized state to another proceeds by tunnelling effect between localized sites, which becomes phonon-assisted at temperatures comparable to the Debye temperature of the material. When subjected to a high electrical field, electronically conductive glasses may switch reversibly to highly conductive states. These switching mechanisms are also reviewed.

4.3. Diffusion in oxide glass-forming systems

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Of major interest in glass science and earth sciences, the mechanisms and rate of atomic diffusion in oxide glass-forming systems are reviewed in this chapter. Experimentally, diffusivities can be measured directly on the basis of Fick's law or indirectly by electrical measurements. Diffusivity varies with the intrinsic properties of the species (valence and size) and the extrinsic parameters composition (X), temperature (T), and pressure (P). Diffusivity typically increases with T and decreases with P according to Arrhenius laws although activation energies and volumes may depend on T and P . Diffusivity generally decreases with increasing concentration of network formers or increasing polymerization/viscosity. Atomistic simulation has emerged as an alternative tool for investigating diffusion, with room for improvement in data accuracy. Interatomic interactions, which hold the key to

understanding diffusion mechanisms and diffusivity trends, have not been fully unravelled. In that regard, first-principles molecular dynamics advanced to the glass transition temperature may lead to future breakthroughs.

4.4. Chemical diffusion in multicomponent glass-forming systems

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In most industrial and natural glass-forming liquids, existing chemical heterogeneities exhibit large concentration differences for several components compared with the surrounding medium, which evolve over time. This general situation is referred to as *chemical diffusion*. In this chapter, we show that the formalism of Fick's laws is not valid in its simplest form for any glass forming liquids. A more general yet more mathematically involved description of diffusion is thus required. In addition, it will offer powerful insight onto the microscopic reactions determining the compositional pathways followed by molten systems on their ways to homogeneity. Available data for silicate systems reveal strong couplings between network-forming and modifying cations. Hence, they suggest that chemical diffusion in complex melts may be reasonably well described with a limited number of exchange reactions identified in ternary systems.

4.5. Thermal diffusivity and conductivity of glasses and melts

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Heat transfer within a phase is characterized by its thermal conductivity (k) and thermal diffusivity (D), which are mutually related by $k = D\rho C_p$ where C_p is the heat capacity and ρ

the density. Conduction is the major mechanism up to about 800 K, above which ballistic radiation has to be taken account and prevails in transparent materials. Experimentally, care must be taken of strain, bubbles or crystallites that alter these properties. High-temperature laser-flash measurements are far more accurate for D than contact methods are for k , because spurious radiative transfer can be removed. For glasses, D decreases as temperature increases above room temperature and then reaches a plateau that is followed for some glasses by small increases up to the glass transition temperature. In contrast, thermal conductivity of glass increases with temperature because the heat capacity rises faster than the thermal diffusivity falls. At the glass transition, however, both D and k decrease. The reason is that structural disorder, which begins to increase markedly at the glass transition, hinders heat transport. For melts, D decreases with increasing polymerization but the temperature dependence of D and k is not well constrained as a result of experimental uncertainties. To understand better thermal transport of glasses and melts, more measurements should be made under extreme conditions along with inter-laboratory benchmarking, utilizing samples of identical composition, texture and thickness.

4.6. Atomistic simulations of transport properties

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Transport properties, especially, diffusion coefficients in melts and glasses can be well characterized by molecular dynamics (MD) simulations. Methods to examine dynamics of glasses or ions in glass-forming liquids including ionic liquids are thus explained and mainly illustrated by results obtained on lithium silicates. The existence of time developments of the mean squared displacements with distinct time regions and the coexistence of fast and slow atoms/ions is usually found. Common features of “dynamic heterogeneities” can be either visualized graphically or characterized by some fractal dimensions. Exhibiting both a remarkable decrease of dynamics, the glass transition and the mixed alkali effects are discussed with respect to some characteristics of slow dynamics.

V. Chemical properties

5.1. Chemical analyses and characterization of glass

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Standard analytical methods for the determination of the chemical composition of glass are reviewed and their advantages and limitations pointed out. For major elements, X-ray fluorescence spectroscopy offers a high level of reproducibility whereas inductively-coupled plasma optical-emission spectroscopy extends analyses to the trace levels allowing for quantitative analysis of environmentally relevant and coloring elements. Atomic-absorption spectroscopy is applied less frequently today. As required by certain pharmaceutical standards, however, it still addresses specific issues such as the determination of arsenic via its hydride-generation variant. The description of fading out methods such as gravimetric and titrimetric methods is restricted to their relevance to modern glass characterization. The same applies to photometric and ion chromatographic methods. Although it has not yet found widespread use in industrial glass analytics, the innovative simultaneous atomic-absorption spectroscopy is also briefly described in view of its importance in fundamental research. Different methods for detection of trace elements, including B, Fe(II) and F, are discussed. The determination of resistance to chemical attack is also treated, as well as the analysis of defects by micro X-ray fluorescence, scanning-electron microscopy with energy-dispersive X-ray spectroscopy and laser-induced breakdown spectroscopy.

5.2. Phase equilibria and phase diagrams in oxide systems

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Glass production usually involves melting of a mixture of solid starting materials. Although typical glasses are homogenous, liquid immiscibility is common in a broad range of glass-forming melt compositions. This chapter thus reviews crystal-liquid and liquid-liquid phase transitions and equilibria relevant for glass making and research. The principles of chemical

thermodynamics, and especially the concept of Gibbs free energy and the Phase rule are used to predict the direction of chemical reactions and the stable state of a system of a given chemical composition at given pressure and temperature. Phase diagrams then display in a graphical form melting/crystallization and mixing/unmixing relationships in temperature-composition (T - x) coordinates. Binary (two-component) phase diagrams showing liquid stability field and its relationship to crystal phases are the simplest diagrams relevant to glass making. The topological types of the binary diagrams are primarily defined by mutual solubility of the components in liquid and solid states. With an increasing number of components, the basic types of phase equilibria remain the same so that ternary diagrams and diagrams for systems with a greater number of components can be viewed as various combinations of binary topologic relationships. Phase equilibria in binary systems of silica with the oxides of alkalis and alkaline earth elements, and the ternary systems Na_2O - CaO - SiO_2 and Na_2O - B_2O_3 - SiO_2 are discussed in more detail in view of their particular importance for glass production.

5.4. Nucleation, growth, and crystallization in inorganic glasses

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We present an overview of the basic phenomena and key theoretical concepts of crystal nucleation and growth in glass-forming liquids. Theoretical predictions of crystal nucleation rates, growth rates, and overall crystallization kinetics regarding the Classical Nucleation Theory (CNT) and the Johnson-Mehl-Avrami-Kolmogorov (JMAK) approach are discussed and compared with experimental data. Most of the experimental results reported for crystal nucleation kinetics in glasses agree only qualitatively with the theoretical predictions of CNT. In this chapter, different possibilities are described that also allow for a quantitative

agreement between experiment and theory. This overview is then completed by presenting conditions for any liquid to vitrify upon cooling or the circumstances in which crystallization is expected to occur. In addition to well-established concepts, relevant open problems are discussed briefly, such as the applicability of different nucleation and growth models, the validity of the Stokes-Einstein-Eyring equation to describe diffusion phenomena that control crystal nucleation and growth in glass-forming liquids, the applicability of the Stefan-Skapski-Turnbull relation to estimate the crystal nucleus-liquid interfacial energy, and other concepts that are expected to be of great interest for future research in this dynamically developing field.

5.5. Solubility of volatiles

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The volatiles in silicate glasses and melts considered are H₂O, H₂, CO₂, CO, CH₄, N₂, NH₃, SO₂, S, H₂S, F₂, Cl₂, and the noble gas series He-Xe. Their solubility typically increases with pressure at high temperature. It can depend significantly on the chemical composition of the silicate with as much as an order of magnitude or more change for given temperature, pressure, and bulk silicate composition. These volatile components dissolve either in a nonreactive molecular form, or interact with the silicate thus changing its structure and affecting its physical and chemical properties. In many instances, reactive and nonreactive species coexist in an equilibrium state that also depends on the whole set of intensive variables. For H-containing volatiles (water, methane, ammonia), the silicate structure becomes depolymerized via formation of OH, CH₃, and NH₂ groups that may replace oxygen in silicate tetrahedral building blocks. For carbon dioxide, CO₃ groups are formed and the silicate can become polymerized. For nitrogen and carbon, redox conditions also affect speciation and, therefore, the equilibria between reactive and nonreactive species. Halogens also form complexes with the silicate components thus affecting the structure and properties of halogen-containing silicate glasses and melts. Noble gases and molecular N₂ and H₂ are in contrast nonreactive and occupy cages in three-dimensionally interconnected structures. Their

solubility is a positive function of availability of structural cages. It also increases with decreasing molecular size or atomic ratio.

5.6. Redox thermodynamics and kinetics in silicate melts and glasses

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Redox reactions in silicate glassmelts and glasses are considered from two, end-member kinetics perspectives. Open-system redox involves long-distance (*i.e.*, far beyond the atomic scale) chemical diffusion as the glass/melt evolves towards equilibrium with the external environment. Closed-system (or internal) redox involves relatively short-range (near-atomic-scale) chemical diffusion as the redox potentials of component cations interact, particularly during quenching. The thermodynamics involved are conceptually straightforward and are usefully considered using Ellingham-type diagrams. Practically—particularly for closed systems—the difficulty in designing or understanding redox behavior is ascertaining the activities of oxide components and their sensitivity to temperature (\pm pressure). Redox dynamics are strongly influenced by heterovalency, which effects electronic conductivity that decouples all ionic fluxes. The reaction morphology, though, frequently can be used to discern the redox dynamics for the case of open systems. Examples presented include float processing of glassmelts and oxidation of glasses as open systems and glassmelt fining and glass coloration as closed systems.

5.7. Optical basicity: Theory and application

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The concept of optical basicity (A) is particularly suited to binary oxides and oxidic network materials such as silicates to characterize the acid/base nature of glasses and melts and to account for the complexation of metal cations by a variety of anionic frameworks. It originates from chemical bonding studies on the interaction between donor oxygen atoms and

probe ions, such as Pb^{2+} and Tl^+ , and enables the establishment of the *optical basicity scale*, from shifts in the ultraviolet (UV) frequencies of these probes. Correlation of A with chemical and physical properties allows trends to be related to chemical constitution. As a consequence, optical basicity finds application in such areas as glass science and technology and the refining properties of metallurgical slags. The development of non-invasive methods for obtaining A , coupled with probe ion data, allows for a chemical bonding description of glass and of sites that are available for metal ions, whether field driven or static. It also apparently explains abnormal variations with composition, for example, in borate glasses, and emphasises the importance of π -bonding in oxide systems. Optical basicity extends to other media, for example, fluoride-oxide glasses, chloride melts and sulphides.

5.8. The glass electrode and electrode properties of glasses

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The glass electrode was invented in 1909 as an analytic instrument right before the pH concept was devised to characterize the acid-base character of a solution in terms of its H^+ concentration. Since then glass compositions have been optimized to make the instrument more sensitive, versatile and precise so that it could be used not only in the laboratory, but in an ever growing variety of industrial and natural contexts. As indicated by its name, the glass electrode is an electrochemical instrument whereby an electromotive force is produced when two solutions having different ion concentrations are interconnected. Even though mainly used to measure pH, a glass electrode can also determine the activity of monovalent cations or redox potentials, and even the structural role of network-former and modifier cations. Beginning with the thermodynamic ion-exchange treatments proposed by Nikolskii and Eisenman, the theory of the glass electrode has been refined over the years to account for the complex hydrolysis-condensation reactions and interdiffusion phenomena that take place within the glass membrane and near the glass-solution interface. In the theory recently proposed by Baucke, equilibrium at the glass/solution boundary is described as a dynamic one not only in terms of thermodynamics, but also of electrochemical kinetics. Further work is

still needed, however, to account consistently for all the phenomena involved, including the effects of glass composition on electrode properties or nonequilibrium factors in glass-solution interactions.

5.9. Electrochemistry of oxide melts

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Various electrochemical methods are applied to glass melts at high temperatures. Simple potential measurements are suitable for the determination of the oxygen activity. Because a prerequisite is a high ionic conductivity at the temperatures at which the measurements are carried out, a certain concentration of highly mobile cations like alkalis is required. The equilibrium thermodynamics of polyvalent ions with oxygen can be measured with methods such as square-wave-voltammetry. Besides, voltammetric methods enable mixed diffusion coefficients of polyvalent species to be determined. The thermodynamics and diffusion of iron, tin and copper have for instance been studied in numerous compositions, allowing models for the incorporation of the respective ions to be derived from the dependence of these parameters on chemical composition. Voltammetric methods can also be used for quantitative chemical analyses in melts containing more than one redox pair. As for impedance spectroscopy, it is a versatile tool to study redox equilibria, diffusivities and also adsorption phenomena of redox species at the electrodes. In principle, electrochemical methods can also be applied to any melt composition including borosilicate, borate and phosphate melts as long as the ionic conductivity is high enough.

5.10. Glass-metal interactions

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Interactions between a metal and a molten glass involve two main phenomena, namely, sticking and corrosion. A physico-chemical approach is proposed here to study and understand the influence of the relevant parameters on these interactions: temperature (which controls kinetics and reactivity), glass composition (as basicity controls oxo-complexation), oxygen partial pressure (which controls redox reactions), surface state and nature of the materials. The main experimental techniques allowing the characterization of the interactions are presented. Wetting can be measured by the "transferred drop" version of the sessile drop technique. The combination of *post mortem* analyses (metallographic observations) with *in situ* measurements (electrochemical techniques) provides complementary thermodynamic and kinetic information on the interaction mechanisms. Corrosion of metals in molten glass being an important issue, the behaviour of noble metals, most common metals and alloys is also reviewed. The materials exhibiting the best resistance against molten glass corrosion build a covering, adherent and homogeneous oxide layer. As the durability of this protective layer is determined by the competition between its growth and its dissolution in the melt, the oxide solubility in the melt should be as low as possible under the conditions of interest.

5.11. Durability of commercial-type glasses

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Although modern commercial glass compositions are usually optimized to have the best possible chemical resistance under ordinary conditions of use, problems are still occasionally encountered during storage and transportation or under various extreme conditions. Whether liquid or vapor, water is always at the origin of the problem. Depending on the pH of the solution, corrosion proceeds either by exchange of H⁺ for network-modifier ions or by breakage of Si-O-Si linkages by OH⁻ ions. Usually the thickness of the resulting leached layer

is limited to a fraction of a micron, but it can exceptionally reach several microns. The consequences are typically an alteration of the optical aspect of the glass, a loss of its transparency and even a degradation of its mechanical properties. These effects are particularly observed after long-distance transportation or long-term storage in confined or warm and humid atmospheres. After production, precautions are thus taken to protect flat or container glass surfaces from water corrosion.

5.12. Mechanisms of glass corrosion by aqueous solutions

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Abiotic mechanisms of chemical alteration of glass are discussed in terms of the two principal theories currently existing. The first is the traditional leached-layer model, which is based on solid-state volume interdiffusion of preferentially leached cations from the glass with hydronium species (H_3O^+) from the bulk solution. This results in the formation of a so-called cation-leached layer that is characterized by broad, diffusion-like chemical depth profiles extending from the surface to the underlying pristine glass. The second theory is relatively new and postulates that glass corrosion is controlled by coupled interfacial dissolution-reprecipitation (CIDR). This mechanism is based on coupled interfacial chemical reactions that take place within a thin fluid film at the glass interface, resulting in a reprecipitated surface layer having a very sharp interface with the pristine glass substrate. Studies from the literature are discussed and critically analyzed to illustrate the application of these two competing theories to borosilicate glass alteration in the laboratory. Finally, the main parameters influencing glass corrosion kinetics are discussed, including those that lead to decreasing rates as a function of reaction progress.

Section VI. Glass and light

6.1. Optical glasses

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This chapter provides a brief overview on the aspects of glass composition and structure that account for the interactions of glass with electromagnetic radiation. The focus will be put on the visible region (relevant to traditional optics), the higher energy ultraviolet and the lower energy infrared radiation. The relevant optical properties each type of traditional optical component will be discussed and how the composition or structure might be adjusted to alter favorably the relevant properties. For each component, typical applications will be reviewed. Any other property potentially relevant to that application, which could also be affected by the adjustment for optical response, will be addressed.

6.2. The color of glass

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Glass coloration is determined by various processes of which the most common imply transition elements through crystal-field effects. A large diversity of original colors largely stems from the peculiar structural properties of transition elements in glasses such as unusual coordination numbers (*e.g.*, 5-coordinated Ni^{2+} and Fe^{2+}) or non-random distribution within the glass structure, which themselves depend on overall chemical composition. Molecular-type charge-transfer processes or electronic excitations within nanophases are other efficient coloration mechanisms, though less sensitive to the details of the glass structure. In addition, attention has to be paid to intervalence charge transfers, which are a direct consequence of a heterogeneous distribution of transition elements in the glass structure. By adjusting elaboration conditions, formulation, melting and fining, it is possible to control transition element speciation and, therefore, glass coloration. A broad range of glass colors can be obtained in this way, which represents a nice application of the structure-property

relationships in oxide glasses. As a result, prediction of color from chemical composition, melting and fining parameters can be made routinely for basic and specialty glasses.

6.3. Photoluminescence in glasses

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The present chapter provides an introduction into the phenomenon of photoluminescence in glasses. Following the presentation of some examples, fundamental aspects will be elucidated. This includes the consideration of photoluminescence as a process of inelastic light scattering, and the nature of the underlying electronic transitions. From the perspective of glass chemistry, the focus will be on the two most prominent groups of optical activators, *i.e.*, rare earth and transition metal ions. More exotic species will also be mentioned as far as they have reached some importance in glassy materials. Finally, an overview will be provided on selected applications, in particular, laser gain media in the forms of bulk glass and optical fibre.

6.4. Optical Fibers

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This chapter provides an overview of glass optical fibers. Particular attention is paid to the materials from which they are made, the manufacturing processes used for their fabrication, conventional and specialty fiber designs, and selected applications of most significant present and future utility. More specifically, whereas silica-based optical fibers will be the dominant focus owing to their commercial maturity, infrared fibers based on heavy metal oxide, fluoride, and chalcogenide compounds will also be reviewed. Industry-accepted chemical vapor-deposition methods are discussed as are traditional batch and melt methods of glass

preparation as well as approaches to fiber drawing. The nature of light propagation in conventional core/clad fiber geometries are noted along with the attributes of more sophisticated photonic crystal and microstructured optical fiber designs. Lastly, the uses of optical fibers in communications, defense, biomedicine and manufacturing are highlighted.

6.5. Fluoride and chalcogenide glasses for mid-infrared optics

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An overview is presented in this chapter of non-oxide glasses containing heavy elements, *i.e.* fluoride and chalcogenide glasses, whose most interesting feature is that their optical transparency extends far in the mid-infrared. For practical applications, the first points needing to be discussed are how glasses are actually formed in these unusual systems and how their structure can be determined, in particular with ^{77}Se solid-state NMR, and depicted by models. Next are addressed the issues of shaping the glass for photonic devices, molding lenses for thermal imaging devices such as night vision camera, and manufacturing fibers for active applications such as fluoride fiber laser and optical amplification, as well as for infrared light guiding. Finally, bio-medical sensing will be discussed as based on mid-infrared evanescent-wave spectroscopy through the large transmission window of chalcogenide waveguides.

6.6. Optoelectronics: Active chalcogenide glasses

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This chapter aims at providing an overview on the concepts and applications of chalcogenide compounds in optoelectronic glasses. Two main themes are (i) chalcogenide glasses doped

with rare-earth ions for active photonic devices and (ii) optoelectronic glasses containing chalcogenide quantum dots. Compared with oxide glasses, chalcogenides possess low multiphonon relaxation, which leads to enhanced near- and mid-infrared emissions from rare-earth ions. In addition, chalcogenide quantum dots yield size-tunable optical properties thanks to quantum confinement effect. As embedded in oxide glasses, they provide potentials for the visible and near-infrared optoelectronics. Fundamental concepts and important achievements in the emission properties and local structure of rare-earth ions in chalcogenide glasses are discussed along with the optical properties and fabrication methods of glasses containing quantum dots are introduced. These chalcogenides in glasses can be used for fiber-optic amplifiers, mid-infrared lasers and color converters.

6.7. Modification technologies of glass surfaces

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Glass surface technologies can be categorized in three groups: (i) removal of material by mechanical, optical or thermal treatment, (ii) exchange by diffusion of glass components with the environment, (iii) addition of material by a coating process (Ch. 6.8). All are applied in industrial praxis. Which is used depends on the properties needed; in addition new ones are under development. This chapter describes the fundamentals underlying the processes in the first two categories and explains the choices available. Methodologies, such as cleaning, polishing, structuring of glass surfaces, ion exchange processing and thermal toughening, will be explained. In the glass community over the last two decades, the term “added value” has dominated discussions of current products. For future applications, most, if not all, relevant added value processes will thus use technologies that modify the surface and create new, and sometimes extraordinary properties.

6.8. Thin-film technologies for glass surfaces

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Although surface modifications have a long tradition in glass production, the globally intensifying nature of research and technological development activities on glass surfaces and coating technologies creating a new dynamics in this field. They are enabling continuous improvement of glass and surface properties together with new functions provided for passive and active smart-layer systems on glass. This chapter summarizes the most important techniques and describes the optical, mechanical and chemical properties that can be engineered. The way in which film composition, thickness and density influences film properties is demonstrated. The properties of technical and commercially significant thin films and thin-film systems on glass, such as electrically conducting oxides, antireflection, low-emissivity coatings and for devices with variable characteristics are discussed in greater depth along with their main applications to optoelectronics and glazing. The range of properties that can be optimized by such approaches is briefly discussed. Examples include traditional products as well as more advanced applications to illustrate how coatings have become vital enablers for advanced glass products and will result in a near future in many new added-value applications.

6.9. Glass for lighting

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Glass was a fundamental component of lanterns to protect the light source from atmospheric agents and the environment from fire without absorbing much light. While keeping the same functions in electric lighting, glass had to satisfy new constraints such as high electrical resistance, thermal-expansivity matching with lead-in wires and other lamp components, resistance to thermal shock (especially for outdoor applications) or absorption of UV radiations emitted in fluorescent tubes, and high-intensity discharge or xenon lamps. Quite

different functions are now assumed in the newly developed solid-state lighting with inorganic and organic light-emitting diodes where glass is either a solid protecting matrix for wavelength-converting phosphors or a transparent substrate for light panels. For these applications not only have new glass compositions been used but also new processes developed to produce flexible and perfectly flat sheet thinner than one hundred microns.

6.10. Screens and displays

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Glass has been widely used for display devices because of its transparency and useful properties. Glasses are hard, transparent materials, with low gas permeability and high chemical durability. These characteristics are essential for making various kinds of display devices. Beginning early in the 20th century Cathode-Ray Tubes has long been at the predominant technology. During the last past decades Flat-Panel Displays have appeared and are currently extensively used in televisions, personal computers, smartphones and a great many other devices. These Liquid-Crystal Displays, Plasma-Display Panels and Organic Light-Emitting Diodes are thus reviewed from a glass perspective. Particularly important is the fact that new glass substrates and frit materials have been developed to meet the requirements of each type of device. Glass sheets are in addition commonly used as optical filters and covers for TVs and touch panels.

Section VII. Inorganic glass families

7.1. Extraterrestrial glasses

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From its birth 4.6 billion years ago to the present day, the Solar System has hosted many environments in which various types of glasses formed by fast cooling of molten silicates. Some of them have been brought down to Earth by meteoroids or sampled by space missions. As illustrated here by three kinds of samples, they provide invaluable insights onto the physical and chemical conditions that governed planetary accretion in a distant past or that are still prevailing within the Solar system. The first are the oldest glasses of the Solar System, which are found in the most primitive meteorites as enigmatic millimeter-sized silicate igneous spherules called chondrules. The second are colorful volcanic glass spherules present in the unconsolidated material at the Moon's surface, which were sampled by Apollo missions. The last are *cosmic spherules*, made up of glass beads resulting from the hypervelocity entry of asteroidal or cometary materials into the earth atmosphere. The reasons why these glasses differ from their terrestrial counterparts are also pointed out, along with their implications for glass science.

7.2. Geological glasses

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Geological glasses cover a wide composition range. The simplest are the almost pure SiO₂ of fulgurites and Libyan desert glass, which have been produced by melting of quartz sand by lightning and the impact or explosion of extraterrestrial bodies, respectively. Tektites have also been produced by extraterrestrial sources but have compositions similar to those of their igneous-rock source. By far the most common glasses are produced by cooling of magmas. The best known are the SiO₂-rich obsidians, which were extensively used and traded over

long distances in Prehistory because of their outstanding properties that result from their fully amorphous nature. Glasses are integral constituents of all volcanic rocks, however, even if their proportion decreases with SiO₂ content. Although vitrification in air becomes impossible at contents lower than about 50 mol %, large glass fractions are nonetheless achieved upon cooling in water. Given the importance of submarine eruptions all along mid-ocean ridges where new ocean floor is created, glasses formed by erupting basaltic lavas are by far the most abundant at the Earth's surface.

7.3. Corrosion of natural glasses in seawater

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Chemical alteration of basalt glasses in seawater ranks as one of the most important global Earth processes, playing a significant role in the terrestrial carbon cycle, the chemical composition of the oceans, and the cycling of major, minor and trace elements between the crust and the mantle. This chapter examines abiotic and biotic processes that drive seafloor alteration of basaltic glasses. Biotic alteration depends on specific metabolic processes that supply energy to microorganisms, and at the same time, serve to breakdown the glass structure. Representative studies illustrate current models of abiotic and biotic basalt glass dissolution. In most cases, the predominant alteration product is palagonite, a secondary surficial phase that grows at the expense of the glass. Its physical and chemical properties indicate how it forms, which in turn is linked to the glass corrosion mechanism. Each study is discussed in light of the two currently accepted corrosion mechanisms: the cation-depleted leached layer model and the coupled interfacial dissolution-reprecipitation (CIDR) model.

7.4. Metallurgical slags

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Slags play an important part in the processing of metals because they carry out many tasks to improve metal quality and reduce process problems. Their physical properties determine how

well these various tasks are performed. They are principally related to two factors, namely, the degree of polymerisation in the silicate structure and the field strengths of the cations present. Knowledge of the factors influencing individual properties allows the slag composition to be optimised for the task in hand. Values of some properties (*e.g.* viscosity, electrical resistivity and reciprocal diffusion coefficient) of metallurgical slags and their temperature coefficients are much lower than those for mineral melts and glasses because they have a less-polymerised silicate structure; this is beneficial to the metallurgical industry since it aids fast kinetics and easy drainage. But good reliable models to calculate property values for slags are needed to provide the necessary input data into mathematical models, which will become ever-more important in optimising process control and product quality in the future.

7.5. Water glass

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Water glasses are alkali silicate glasses or alkali silicate sols made by dissolving the glasses in water or by alternative routes. The liquid water glasses are highly concentrated alkaline, usually sodium or potassium, sols with up to 30 wt. % silica. Monomeric or polymeric molecules and anions as well as silicate colloids are the silicate species in concentrated liquid water glasses. The structure of the concentrated systems can be described as a dispersion of silicate colloids in alkali silicate solutions saturated on a molecular level. Water glasses are for instance used as source of silica or alkalinity in chemical processes, as precursor for silicate synthesis or as binder.

7.6. Borosilicate Glasses

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Borosilicate glasses are ubiquitous in modern science and technology. What we generally consider a well-established system in glass science is actually quite young and has a fascinating history. The discovery and commercialization of borosilicate glasses is widely credited to Michael Faraday and Otto Schott, respectively. Since their inception in the 19th century, these materials have been exploited for their thermal properties and chemical durability (Duran[®] and Pyrex[®]). They are characterized by significant phase separation, both as an attribute (*e.g.* Vycor[®]) and a challenge in glass fabrication, and remain the subject of extensive experimental and theoretical examination of glass structure at the short- and intermediate-range length scales. Along with an overview of commercial borosilicate glasses, this text addresses structure/property relations, short- and intermediate-range structure as determined by NMR and other spectroscopies, as well as the impact of both temperature and pressure on the structure of these glasses. This discussion is concluded with several key scientific questions and opportunities which are typical of glasses in general. Owing to the impact of borosilicates on humanity, however, these are critical for advances in understanding and usage of these important materials.

7.7. Glass for pharmaceutical use

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Chemical durability, gas impermeability, excellent resistance to moderate thermal treatments and easy inspection make glass an important material in pharmacy. Hence, the Pharmacopoeia's requirements for glass containers are first illustrated in this chapter and the most common glass types are defined. The current glass-tubing production processes, as well as the conversion steps to obtain containers from glass tubes, are briefly described. The mechanical and chemical resistance most outstanding properties offered by borosilicate

glasses are described, including the effects that improper forming or handling may have on their performance. The interaction with aqueous solution and the effect of pH is described, the action of buffers and organic acids like citric acid and the effect on the outmost inner surface of the containers is highlighted. Secondary treatments of both the inner and outer surface to improve the chemical durability and mechanical resistance are also covered with considerations on their efficacy. The surface interaction with drugs is considered with a particular care to phenomena like glass delamination, particulate matter formation and the release of leachables and extractables that may heavily impair the inertness of the glass container. Finally, the chapter examines some perspectives on the future of glass containers for parenteral packaging, focusing on innovative solutions aimed at guaranteeing the highest quality standards.

7.8. Oxynitride Glasses

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Oxynitride glasses form in a number of M-Si-Al-O-N systems where up to 30 equivalent % (eq. %) nitrogen can be accommodated. Elastic modulus, hardness, glass transition temperature (T_g) and viscosity all increase linearly with nitrogen content whereas thermal expansion coefficient decreases. For example, for glasses with constant cation ratio (in eq. %) of 28Y:56Si:16Al, as 17 eq. % oxygen is replaced by nitrogen, Young's modulus increases by 35% from 112 to 149 GPa, microhardness by 16% from 8.8 to 10.2 GPa, viscosity by 2 orders of magnitude and T_g from 940 to 990 °C. These changes result from increased crosslinking as N substitutes for oxygen, leading to a more rigid glass network, which is made up of SiO_4 , SiO_3N and SiO_2N_2 tetrahedral structural groups. The effect of nitrogen on properties is much greater than that of cations. For rare earth lanthanide-Si-Al-O-N glasses of constant stoichiometry, viscosity, Young's modulus and T_g increase linearly with decreasing ionic radius and increasing cation field strength. As with silicate-based oxynitride glasses, the properties of phosphate oxynitride glasses increase with nitrogen content. In crystallisation studies, suitable two-stage heat treatments for nucleation and growth yield glass ceramics with significant increases in strength over the parent glass. The substitution of oxygen by both fluorine and nitrogen allows melting temperatures to be reduced while maintaining the higher

elastic modulus and hardness conferred by nitrogen, which might allow exploitation in specialist applications.

7.9. Phosphate glasses

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Phosphate glasses have been well-established materials since the early 1800s but are largely unknown by the wider community, being lost behind the general descriptor of ‘glass’. They have several significant attributes, notably an exceptional ability to form homogeneous glasses with large amounts of modifier oxides, including in particular nearly 20 mol% of rare earth oxides; wide and adjustable optical transparency between ~200 and 1000 nm; expansion coefficients higher than 20×10^{-6} ; and an extremely variable solubility in water, which ranges from $\sim 10^{-4}$ to $10^{-9} \text{ kg m}^{-2} \text{ s}^{-1}$. These attributes have been key to the development of applications in areas as diverse as water treatment, food, high-energy lasers and nuclear waste containment. Research in phosphate glasses has accelerated in the last two decades, with in particular potential new applications in absorbable medical devices and in solid-state electronics and lighting.

7.10. Bulk metallic glasses

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The formation, structure, properties and characterization of metallic glasses produced from the liquid state by casting or water cooling are reviewed in the present chapter. The structure, general physical, thermal, mechanical and magnetic properties of these materials are also

discussed. Crystallization of bulk glassy alloys leads to the formation of the composites containing crystalline or quasicrystalline particles. Some of these composites possess a better combination of mechanical properties than those of fully glassy or fully crystalline alloys. For example, crystalline phases play a very important role in ductilization of bulk glassy alloys. Nanostructured ferromagnetic alloys and glassy-nanocrystal composites possess good soft magnetic properties.

7.11. Glass-ceramics

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Glass-ceramics are materials produced by a two-fold process whereby a glass is first formed and then partially crystallized by an appropriate subsequent thermal treatment. With respect to glass materials, glass-ceramics acquire a complex microstructure during the crystallization step that gives them specific properties and makes a wide range of applications possible. The most widely used systems are lithium aluminosilicates, magnesium and zinc aluminosilicates, lithium silicates, and phosphates for which mechanical properties, resistance to thermal shock, chemical durability and/or transparency have been optimized. Although some glass-ceramics can be prepared through homogeneous crystallization, heterogeneous nucleation is generally required to precipitate the intended crystalline phases. With the exception of the surface crystallization used to produce some materials, heterogeneous crystallization generally requires the use of nucleating agents to ensure a uniform distribution of crystals in the bulk. The main nucleating agents are oxides (TiO_2 and ZrO_2), fluorides, or colloids of noble metals such as Ag, Pt, and Au. Either they precipitate themselves and create nucleating sites for the main crystalline phase, or they first induce a phase separation such that one of the new amorphous phases is more prone to crystallization than the starting glass.

Section VIII. Organically related glasses

8.1. Biogenic silica glasses

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The yearly world production of biogenic silica of over 20 billion tons play a crucial role in the global carbon cycle and can even affect atmospheric CO₂ concentration. About three fourth of this amount is produced in seawater by diatoms, which are small photosynthetic algae, and to a much lesser degree by the radiolarians of the zooplankton or by sponges. The remaining one fourth is produced on land by plants from most groups as concretions named phytolithes. This production has a definite economic importance in terms of diatomite products and of the silica that can be recovered from the ashes of plants such as rice. This biological production involves room-temperature polymerization of silicic acid molecules Si(OH)₄ forming at very low concentration in water through silicate dissolution. It has opened wholly new areas in materials science as nanostructured biogenic glasses exhibit very interesting mechanical and optical properties that is the source of a bio-inspiration in sol-gel processes. The frustules of diatoms can be used as precursors for making electroluminescent devices and solar cells and they have a 3-D hierarchical distribution of their pores that may ensure photonic-crystal properties. The soft conditions associated with this process lead to the formation of hybrid nanocomposite materials in which organic- and inorganic components are mixed at the molecular scale.

8.2. Sol-gel process and products

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As alternatives to traditional melt-quenching, sol-gel methods are wet chemical routes based

on colloidal chemistry techniques that are used to synthesize glassy, hybrid (organic-inorganic) and crystalline materials at relatively low temperatures. They are reviewed in terms of the main steps of solution preparation, ageing, forming, drying and sintering into dense nanoparticles, glassy/ceramic films or bulk materials, with particular emphasis on dip-coating and spin-coating deposition of films. This review is followed by a systematic consideration of the advantages and drawbacks of these methods. The former include the low-temperature nature of the process, the preparation of homogeneous non-crystalline solids in unusual composition ranges and the fabrication of special products like nanoparticles, powders, films and fibers with improved purity and homogeneity. As for the drawbacks, they are mainly the cost of raw materials, shrinkage during processing, and the difficulties of eliminating residual hydroxyl species or obtaining large monoliths. Then, the most representative products and applications at present are reviewed in the automotive, architectural, ophthalmic, electronic, household and optical domains. The final section focuses on new perspectives in the field of sol-gel science and technology, for example new glasses, more reproducible preparation conditions, increasing use of spray- and roller-coating methods for film deposition, ink-jet and 3-d printing and biomedical applications.

8.3. Silica aerogels

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Silica aerogels are highly porous, predominantly mesoporous solids with an open network of amorphous silica nanoparticles produced by sol-gel processes. The materials are made from waterglass or silicon alkoxide precursors through gelation, aging, optional hydrophobization and supercritical or ambient-pressure drying. Silica aerogels possess a range of exceptional properties such as high vapour permeability, low density (down to 0.002 g/cm^3 , but much more commonly around 0.1 g/cm^3), high specific surface area ($500\text{-}1000 \text{ m}^2/\text{g}$), ultra-low thermal conductivity ($12\text{-}18 \text{ mW}/(\text{m}\cdot\text{K})$) and tuneable hydrophobicity. Potential applications include CO_2 capture, oil-water separation, catalyst support or Knudsen pumps, but by far the most established use is as thermal superinsulation for the oil-and-gas and construction sectors with a market size of hundreds of millions of US \$. Technical innovations in

production technology and the entry of new producers are expected to lead to a significant reduction in cost and accelerate an already substantial market growth in the near future.

8.4. Bioactive Glasses

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Bioactive phospho-silicate glasses release ions when in contact with physiological solutions and show surface reactions leading to the formation of a biomimetic apatite layer. This surface layer allows for protein adhesion, cell attachment and proliferation and formation of a strong interfacial bond between bioactive glass and bone. In addition, the ability of bioactive glasses to degrade *in vivo* makes it possible for them to be replaced by new bone and, thus, to aid in the regeneration of bone tissue. These reactions are possible owing to the highly disrupted structure of bioactive glasses, containing large concentrations of modifier ions and nonbridging oxygens. Bioactive glasses have been used clinically since the mid-1980's, mainly to treat bone defects. However, their mineralising properties have led to their use in oral care products for the treatment of sensitive teeth and the remineralisation of enamel.

8.5. Dental glass-ceramics

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Glass-ceramics have become high quality restorative materials following the introduction of a mica-based product in the 1980s, which could be not only molded but also machined. As first reviewed in this chapter, various constraints have to be respected in terms of machinability, radio-opacity and optical, thermal and chemical properties for dental restorations as dental inlays, onlays, veneers or bridges. Three types of products will then be presented in more detail: leucite [KAlSi₂O₆]-type and lithium disilicate [Li₂Si₂O₅] glass-ceramics, followed by

glass-ceramics based on the precipitation of phosphate crystals. Finally, the needs of the rapidly developing field of digital dentistry for an enhanced quality of glass-ceramic materials will be briefly mentioned.

8.6. Relaxation processes in molecular liquids

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The dynamics of molecular liquids as they are cooled from the boiling point down to the glass transition temperature is reviewed from various broadband techniques at ambient and elevated pressures. This discussion includes the search for growing length scales as revealed by sophisticated experimental and computational approaches. Furthermore, we deal with dynamically asymmetric binary glass-forming liquids, which have become an interesting field of research as they not only possess numerous applications, but also show a rich dynamical scenario, including the existence of two glass points and intrinsic confinement effects. In addition, we discuss secondary relaxations, which emerge when approaching T_g and persist in the glassy state. Finally, glassy crystals are considered as model systems for cooperative dynamics.

8.7. Physics of polymer glasses

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Polymers consist of macromolecules, which make their liquid and solid states markedly different from those of ordinary liquids and metals or organic crystals, respectively. The large chemical diversity of macromolecules results in a broad variety of polymeric glasses. Because they have glass transition temperatures in the 150 - 500 K range, polymers are suitable for low-temperature spinning or molding. One of the most striking properties of these liquids is their stress response to strain, which exhibits both viscosity and elasticity components

induced by the random motions of their chains; these are thus characterized by broad spectra of relaxation rates, which control the glass transition process. The structure of glassy polymers can in addition be modified by partial crystallization and/or partial chain cross-linking leading to a polymer network. Typical uses as films, fibers, porous membranes or foams are described, and also ageing processes that affect polymeric glasses over periods extending to several years.

8.8. Introduction to Polymer Chemistry

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Polymers are large, chain-like molecules formed by multiple reactions of small molecules whose broad ranges of properties and uses originate in the diversity of monomers, monomer combinations, and polymer architecture. Polymerisation proceeds either by chain growth, where one molecule after the other is added to the growing chain, or by step growth, where two similarly large molecules react to form a long chain. Whereas polymerisation in bulk seems to be the most economic and ecologic process, it is only used for step-growth. Chain growth in bulk usually suffers from heat-transfer problems and incomplete conversion, leaving too much residual monomer in the final product. As a result, chain-growth polymerisations are frequently run in aqueous suspensions or emulsions, which can be directly sold as latex or easily processed to yield solid products. The properties of polymers in the solid state are mainly governed by factors that control the glass transition temperature, which represents the onset of large-scale cooperative motion of chain segments. Thus, increasing the attractive interactions between chains hampers their mobility and increases T_g as well as mechanical properties. The opposite effect is called plasticization and is frequently used with poly(vinyl chloride) for the production of artificial leather.

8.9. Hybrid inorganic-organic polymers

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Hybrids between inorganic and organic polymers called inorganic-organic polymers (IOP) can be generated for instance by colloidal synthetic routes also known as sol-gel processing or chemical nanotechnology. Their unique character results from their structural units connected on the molecular scale leading to very homogeneous and highly transparent materials. To a certain extent IOP-hybrids combine favorable properties of inorganic glasses and organic polymers. They are synthesized from organically modified silicon and metal alkoxides in a two-step process. Coatings, powders, fibers, bulk materials and composites can easily be generated and are already used in industrial applications. This contribution focuses mainly but not only on coating applications, especially on glass surfaces. Various other applications areas like particles, membranes, bulk materials and composites are also described briefly. Future activities in the field of IOP will encompass advanced production processes like additive manufacturing and the use of biodegradable or biobased precursors.

Section IX. Environmental and other issues

9.1. Structural Glass in Architecture

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In this chapter we review how the brittle nature of glass requires specific attention in the design, manufacturing and construction of point-fitted glass, glass floors and stairs, balustrades and façade fins, glass roofs and walls. These applications in buildings, which go far beyond the traditional framed glazing, are all grouped under the term ‘structural glass’, which has been actively developed since the 1970s. Premature failure has to be avoided through meticulous design and analysis of the overall structural scheme, connections, and failure scenarios. Laminating is the most widely used method to obtain sufficient safety. Thermal prestressing is used to obtain sufficient resistance and to avoid subcritical crack growth. Connecting elements together requires specifically developed details and methods, as glass can typically not be machined on site as most other construction materials. Although connections have generally been mechanical, adhesive connections are more and more applied. A wide range of developments on glass manufacturing, processing and design is under way and will further push the applications in buildings in the future.

9.2. Tempered and laminated glazing for cars

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Flat-glass transformation is dealt with in this chapter through the example of car glazing. The long-standing problem posed by conciliating vision with protection from weather conditions is first reviewed historically. The various functions of car glazing are then described in relation to vision, safety, heat, noise, information display and recycling. We also overview the main manufacturing

steps, namely, cutting, screen printing, forming/strengthening, and functions integration, making clear why a huge added value is brought to the car glass market by these technologies that enable glass to meet ever more and technology advanced demands from both car manufacturers and end users. Finally, new challenges to be met in the future are mentioned.

9.3. Stone and glass wool

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There has been a rapid development in stone and glass wool concerning physical and chemical stabilities, insulating ability, bio-persistence, application, and production technology. In this chapter, we review this development and the recent understanding of the physical and chemical properties of the wool fibres. We also discuss the controlling factors for the crystallization behaviour, high-temperature stability and mechanical properties of the wool fibres. Finally, some perspectives towards improved wool products and optimized fibre spinning technologies are illustrated.

9.4. Glasses for solar-energy technologies

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Glasses are well-established materials for solar energy with rapid payback times and the high environmental compatibility required for sustainable energy concepts. As reviewed in this chapter, glass is not only playing an important role as transparent cover and substrate in various conversion systems producing electricity, heat and fuels from solar radiation, but is also utilized to clean natural resources such as water and air through solar photocatalytic processes at its surfaces. Special attention is paid to the optical properties relevant to the transmission, redirection and collection of solar energy in various conversion systems.

Finally, a look is taken into the future, to the challenges facing glass in solar technologies that are emerging or have already become an integral part of the renewable energy sector during the last two decades.

9.5. Sulfide-glass electrolytes for all-solid-state batteries

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Interest in solid electrolytes based on alkali sulfide glasses for all-solid-state batteries stems from the high electrical conductivity, wide electrochemical window, good formability (processability), appropriate elastic moduli and excellent cycle performance of these materials. In the systems $\text{Li}_2\text{S-P}_2\text{S}_5$ and $\text{Na}_2\text{S-P}_2\text{S}_5$, the electrical conductivity can even be increased by partial precipitation of metastable crystalline phases with high ionic conductivities. Room-temperature conductivities of 10^{-2} and 10^{-4} S cm^{-1} have been for instance achieved for the $\text{Li}_7\text{P}_3\text{S}_{11}$ and cubic Na_3PS_4 -bearing glass-ceramics, respectively. Various methods may be used to optimize electrode-electrolyte contact, namely, sulfide electrolyte coating on LiCoO_2 by Pulsed-Laser Deposition, preparation of nanocomposites by high-energy ball milling, and softening glass electrolytes with electrodes near the glass transition.

9.6. The world of the flat-glass industry

Key milestones, current status and future trends

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As first documented in this chapter by a summary of key milestones, the rate at which innovations have been made in flat-glass production has considerably accelerated from the mid-19th century. In this evolution, four revolutions can actually be recognized, namely, the Leblanc process for production of soda ash, the Siemens continuous furnace, the Fourcault continuous drawing process and, last, the float process in the 1950s. Since then innovation has

mainly shifted to secondary treatment or transformation of float glass. The thermal, mechanical or optical requirements of a great many new applications have been satisfied with coatings, tempering, chemical strengthening or laminating. At the same time, flat-glass production has ceased to be concentrated in developed countries. In two decades, China has by far become the main producer, accounting for more than 50 % of the world output. These trends have been accompanied by very strong competition, which has caused much industry restructuration as a result of a six-fold decrease of the price of flat glass (in constant value) over the last five decades in Western Europe. The flat-glass market is in contrast expanding or will expand considerably not only in China, but also in the Middle East, Africa, South America and especially in India.

9.7. Design and operation of glass furnaces

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Glassmelting furnaces are of different types whose design and working operations are reviewed in this chapter. With the exception of all-electric furnaces, these use fossil fuels for transforming the batch of raw materials into a molten glass ready to be shaped. They consist not only of melters but also of regenerators or recuperators to recover part of the heat of the waste gases. Following a general picture of these two major components, a more detailed description is given for end- and cross-fired regenerative furnaces as well as for recuperative, all-oxyfuel and all-electric designs. Particular attention is paid to means such as electrical boosting for additional, well localized energy input directly into the melt, bubbling implemented to improve thermal and chemical homogenization of the glass in the melting tank, and to the refractory materials employed to optimize construction and operating costs. The electrocast Alumina-Zirconia-Silica (AZS) refractories are particularly important in this respect owing to their excellent high-temperature mechanical properties and their remarkable resistance to chemical attack by molten glasses. After some general empirical rules followed in furnace design are reviewed, the issue of pollutants emitted such as NO_x and SO_x is finally considered in view of the ever stricter nature of current environmental regulations.

9.8. Physics and modeling of glass furnaces

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This chapter is devoted to the basic physics of glass furnaces and their finite-element modeling. Fossil-fuel fired and continuously operated glass furnaces are first treated in their basic function as heat exchangers and chemical reactors, which can be characterized by a relatively small set of key indicators. As an expression of the first Law of thermodynamics, a general heat balance is elaborated in detail. As an expression of the second Law, process irreversibility is then taken into account to determine how furnace performance depends on production rate. The input-output characteristics of furnaces is finally treated in terms of standard models of reactor technology to determine the optimal operating conditions in terms of yield and quality. In the second part of the chapter, results of finite-element modeling of industrial glass furnaces are reviewed. Simulations of residence times for tracers and of temperature profiles in furnaces illustrate the accuracy of the calculations, whereas important information is also obtained on the circulation patterns of the material in melters. The increasing usefulness of these simulations for glass making is thus emphasized.

9.9. Glass cullet: Sources, uses and environmental benefits

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As a *permanent material*, glass can be recycled indefinitely. For a whole cycle returning a container to its original condition after use, every ton of cullet replaces about 1.2 tons of raw materials and avoid the production of 670 kg of CO₂ coming from replaced carbonates, lower energy consumption for melting, and indirect savings in extraction, production and transportation of raw minerals. Whereas on average the current recycling rate is 73 % in Europe and developed countries, cullet recycling could reach 95 % for producing coloured glass container. The availability of cullet of suitably high grade to fulfil the ever increasing quality demanded by the glass-container industry induces treatment plants to increase the cleanliness of their products and, thus, the amount of rejects. Probably only in the U.S. and

Russia is there room for consistent growth if suitable actions are undertaken to activate a sustainable system through better citizen awareness of the waste impact. But developing countries, as well as BRICS, should from the beginning apply the best practices to limit the overall environmental impact of their growing economies. Whereas Authorities must give a definite leverage to the glass industry for making investments possible toward a sustainable Circular Economy, the technology should be improved to cope in almost real time with possible fluctuations in cullet quality and to increase the use of secondary raw materials obtained from the cullet reject.

9.10. Immobilization of municipal and industrial waste

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As introduced in the late 19th century, incineration enables the volume of municipal and industrial waste to be drastically reduced and toxic substances and microbiological agents to be eliminated. In this chapter we review first the combustion process and the three main types of the resulting municipal solid waste incineration (MSWI) residues, namely, bottom and fly ashes and Air-Pollution Control (APC) residues. Aluminosilicate glasses are the dominant phases in MSWI residues, coexisting with a wide variety of silicate minerals, metals, salts and organic substances. The presence of heavy metals in the original materials and the formation of organic pollutants such as dioxins and furans during combustion of these phases are important issues to be dealt both during combustion and in long-term disposal of the waste, hence the great attention paid to the influence on leachability of the chemical composition and nature of the MSWI residues. In this respect, vitrification or glass-ceramisation of ash to produce new usable materials are interesting possibilities for utilization purposes. Along similar lines, incineration is also an alternative to landfill for other high-volume waste (coal ash and blast-furnace ashes, sewage and dredging sludge) and special electronic, asbestos or medical waste.

9.11. Nuclear waste vitrification

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Because of its disordered structure, glass was identified in the 1950s as an excellent material for confining the wide range of elements present in fission product solutions arising from reprocessing of spent nuclear fuel. Glass can actually host most of the radioactivity generated in nuclear power plants. After two decades of research in this area, industrial vitrification lines have been commissioned in most countries involved in nuclear energy. In nuclear containment glass, radionuclides generally form chemical bonds with the glass constituent atoms. The preferred glass formulations are mixed alkali aluminum borosilicates because they combine the possibility of incorporating of a wide range of radioactive elements with a relative ease of synthesis and long-term stability. Vitrification furnaces have been developed for this application. The elements to be immobilized are mixed at high temperature with glass-forming additives to form a glass melt which, after cooling, becomes a chemically durable glass material with low radiation sensitivity. The debate on safe management of high-level waste has converged on deep geological disposal. In addition to thermal and radiation stability issues, the demonstration of long-term glass stability considers the surrounding environment as a key component constraining glass performance.

9.12. The International Commission on Glass (ICG)

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This review explores the origins of the ICG, its constitution and aspirations, together with the individuals and the history that have shaped its development. Its role in the international glass community is explained: its organisational structures; the nature and activities of its technical committees; its congresses and funding; its publications and contribution to education; and the prizes awarded in recognition of services rendered to the Glass community. An analysis of its ambitions, its future directions, concludes the story.

Section X. History of glass

10.1. Obsidian in Prehistory

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Obsidian is a glassy volcanic rock that has been used to make stone tools for two million years. Geological sources of obsidian have been identified in many parts of the world, including on Mediterranean islands; in southeastern Europe, Anatolia and the Middle East; East Africa; northeast Asia and Japan; on islands of southeast Asia, Oceania, and the Pacific; and along the mountain chains of western North America and the Andes of South America. The uniqueness of this stone material led to its distribution or trade over hundreds and even thousands of kilometers. Thanks to the distinctive physical and chemical characteristics of this rock, archaeological studies have successfully traced for more than 50 years the sources of obsidian artifacts to reconstruct prehistoric trade patterns. In addition, microscopic studies of the wear patterns on the edges of obsidian tools help to identify their usages on different materials, while their production can be dated through measurements of their hydration layers. Today, a number of analytical instruments may be used to determine the specific source or subsource of obsidian artifacts; the development of low-cost portable non-destructive X-ray fluorescence spectrometers has enhanced tremendously the number of artifacts studied in museum collections around the world. In the western Mediterranean, as well as the Near East and Latin America, obsidian analyses have revealed distribution patterns which changed over time, inferring developments of more complex socioeconomic systems, and differences in the specific purpose and usage of obsidian, especially when comparing residential and ritual contexts.

10.2. Ancient Glass, Late Bronze Age

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Glass is first produced in a regular way in the mid second millennium BC, where production appears to begin in both Egypt and the Near East. How glass is invented is unclear, but it may be derived from other pyrotechnologies, perhaps either metalworking (where the material is manipulated hot, like glass working) or faience making (where all the same raw materials are already in use). By 1400 BC, glass is an important prestige product, exchanged over long distances, and is used as a precious stone, perhaps having the same high values. Late Bronze-Age glass is a soda-lime silicate composition, made from crushed quartz or quartzite pebbles, a plant-ash flux and a colorant. Colorants include copper (blues and red), cobalt (dark blue), lead antimonate (yellow), calcium antimonate (white), and manganese (purple and black). Sometimes these colorants are mixed, for example lead antimonate and copper making a green glass. Since glass is such an important material in this period, attempts have been made to provenance it back to the place it was made. Various techniques have been tried, the most important of which are trace element analysis by ICPMS and isotopic analysis, especially of strontium and neodymium isotopes. This work has demonstrated from where important glass finds, such as the Ulu Burun shipwreck, might have originated and has argued against the production of glass in the Greek world in this period.

10.3. Roman Glass

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Roman glass technology was based on soda-lime-silica glass made by fusing a two-component mixture of naturally occurring sodium carbonate from Egypt with quartz-rich sand, which contained calcium in the form of beach shell or limestone. The primary glass material was fused in tank furnaces with capacities in excess of several tonnes in the eastern

Mediterranean, broken up into chunks and exported across the Empire to be fabricated into vessels, sheets and beads in many secondary workshops. Colourant technology involved the use of opacifiers based upon antimony and later upon tin, whereas pinks and reds based upon gold nanoparticles appeared in the fourth century CE. Recycling was common practice and becomes increasingly apparent from the sixth century. There is a gradual decline in the soda content of glass throughout the millennium, and the use of Egyptian natron as a flux, diagnostic of the Roman tradition, appears to have ceased in the ninth century.

10.4. Glass and the philosophy of matter in antiquity

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Ancient glass recipes transmitted by Mesopotamian and Egyptian civilizations reveal that craftsmen thought that both glass and metals contained a certain amount of water that made possible to melt them. In Greece the first natural philosophers eventually attempted to classify glass as a chemical substance and to use it as an explanatory model for a better understanding of a wide range of natural phenomena related to the philosophy of matter. During the Hellenistic progress in glass making helped to tighten the bridge between alchemy and glass technologies. Byzantine culture then preserved in Constantinople both the secrets glass making and the alchemical corpus of writings that were finally transmitted to both Islam and the Latin West. Hence, the discovery of glass in ancient civilizations had a strong cultural and scientific impact because it did not represent only a breakthrough in chemical technology. It also introduced innovative ways of understanding the power of man over matter and engendered a surprisingly rich variety of artifacts.

10.5. Ancient glassworking

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Ancient glassworking designates the techniques used to shape glass into objects from about 1550 BCE until the 7th c. CE in western Asia, the Mediterranean basin and Europe. Before the discovery of inflation, shaping did not require the use of hot molten glass. Core-forming,

casting, rotary pressing, casing, and sagging could be performed at lower temperatures. As is common with discoveries, that of inflation towards the beginning of our era was accidental. It began with tube blowing and was then slowly perfected. Decorative techniques included hot work as well as cold working executed by other specialists. Gold glass, cameo glass, and cage cups required special techniques that have been much debated. The blowers, their workshops and the design of their furnace are also discussed before some epistemological reflections are presented on the uses and functions of glass in ancient society and on innovation in glassworking techniques.

10.6. Glazes and enamels

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In the form of glazes and enamels, thin glass coatings are deposited on pottery, glass and metal surfaces for aesthetic reasons and also to tighten porous bodies and harden their surfaces. In this chapter, the preparation, composition, coloration, thermal expansion, micro- and nano-structures of these glass coatings are first surveyed. Attention is in particular paid to the optimization of thermal expansion matching upon cooling and heating, wetting properties and softening temperatures. In addition, the thinness of the coatings requires specific colouration techniques by pigments or metal nanoparticles, which is why a very large variety of compositions had to be used throughout the ages. The history of coatings on metal (Celtic, Limoges, and Chinese *cloisonnés* enamels), on glass objects (Roman/Ptolemy to Mamluks and then Renaissance) and on potteries (*terra cotta* [fired clay in Italian], stoneware, fritware, and porcelain) is then reviewed along with their preparation routes (ashes, rocks) and compositions. Technical exchanges, as well as the different techniques used to obtain similar visual effects are addressed with emphasis on the most innovative productions including Tang/Yuan/Song porcelain, Abbasid/Fatimid lustre pottery, Chinese/Vietnamese stoneware and *celadons*, Japanese *Raku*, Iznik fritware, and European soft-, hard- and hybrid-paste porcelains. The chapter ends with the 19th century technical revolution, the Craft and Japonism movements and modern/contemporary production.

10.7. Venetian glass

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Combined with historical sources and recipes of Medieval and Renaissance treatises of Venetian glassmakers, chemical analyses of archaeological finds allow for a good understanding of the evolution of Venetian glass compositions and technology from its origins until the 18th century, i.e., the end of the Venetian Republic. These analyses made for a significant amount of archaeological finds from the Venetian lagoon and towns near Venice give evidence of a production continuity from the Roman time until today in the Venetian area. The transition in technology from natron to plant ash glass in the 9th to 13th centuries, subsequent changes aimed at improving glass quality, and the use of new raw materials throughout the 18th century are documented. The secrets of *cristallo*, the high quality clear Venetian glass, are highlighted, as well as of coloured glasses such as *chalcedony*, *lattimo* and *aventurine* that made the fortune of the Renaissance Venetian glassmaking for two centuries. The consequences of the *façon de Venise* production and the development of new glassmaking centres in northern Europe during the 17th-18th c. for Venetian glassmaking are finally considered: whereas the luxury market was declining, other objects such as small mirrors and beads were mass produced to such an extent that glass production actually doubled.

10.8. Stained glass windows

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This chapter examines the way technological factors have influenced the development of decorative glass windows over the last two millennia, but also emphasizes the role of ecclesiastical institutions, the influence of Christian thinking and, more recently, secularization as drivers of change. First is a consideration of the *crown* and *cylinder* glass-sheet manufacturing processes together with issues such as chemical composition and

resulting chemical durability. This is followed by an analysis of the various ways in which glass has been colored and images generated, including a discussion of the origins and range of available colors, glass staining, painting techniques and the nature of the images created. The transfer of an initial design to a traditional stained glass window made up of small panes joined by lead strips is described. Recent innovations in design and subject matter conclude the presentation.

10.9. Furnaces and glassmaking processes: From ancient tradition to modernity

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After a period of outstanding technical inventiveness during Antiquity, glassmaking furnaces and processes underwent little changes until the early modern period as illustrated by the descriptions left by the monk Theophilus in the 12th century and even by Agricola in the 16th. The main change had been the need to use ashes as a source of flux instead of the much purer natron, which caused a decrease in glass quality until the invention of *crystallo* made in Venice from purer raw materials. As part of the Western economic expansion, the development of glassmaking then induced in England at the beginning of the 17th century the switch from wood to coal in furnaces, which in turn affected the melting operations. This was the time when glazing began to be extensively used in houses, and no longer mostly in churches. Flat glass was still made with the traditional crown and cylinder processes in the same way as hollow ware kept being blown with the old-age methods. At the end of the 17th century, the search for larger and less expensive mirrors led to the invention, by a company that would become known as Saint-Gobain, of a method that combined table casting, grinding and polishing of plate glass. But it was only in the 19th century that all glassmaking operations were radically modified. Relying on the new science of thermodynamics, efforts were made especially in England and Germany by the Siemens brothers to increase the heat efficiency of furnaces by recovering part of the energy wasted through the chimneys, improving combustion with coal gasification, and turning to large tanks instead of small pots for glass melting. Both quality and production costs then benefited from higher and more uniform melting temperatures, faster processes, more durable installations, and reduced labor. Of great

importance was also the fact that tank melting made continuous processes possible at the beginning of the 20th century after machines had been designed to produce flat glass directly and to blow mechanically container glass. Engineering masterpieces were finally designed by Pilkington and then by Saint-Gobain toward producing continuously ground and polished ribbons of plate glass. Ironically, however, this goal was at last achieved in the 1950s at a time when the revolutionary float process, also designed by Pilkington, made at once both the traditional procedures and the distinction between *flat* and *plate* glass obsolete.

10.10. Glass, the wonder maker of science

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Glass made its scientific debuts in the 2nd century AD through the study of light refraction at a time when it was also gaining in importance in alchemy through various kinds of vessels and devices. Understanding that the shape of glass pieces only matters in optical applications much later led to the invention of spectacles in Italy in the 13rd century to relieve farsightedness with converging lenses. The telescope, followed by the microscope, was then invented early in the 17th century shortly after divergent lenses were made to relieve myopia. In the same way that the telescope induced a major change in the representation of the heavens, the microscope revealed a wholly unexpected new world populated by tiny living beings and showing a wealth of unsuspected small-scale details on things familiar. Through Newton's experiments on the glass prism, the nature of light began to be understood at the same time. But optical investigations suffered from the problem of chromatic aberration (Ch. 6.1), which was eventually solved thanks to the new lead-bearing *flint* glass. Chemistry also took advantage of glass not only with a paraphernalia that kept diversifying throughout the ages, but also with the new system that could be built once glass corrosion experiments had firmly disproved Aristotle's theory of transmutations between the four elements. In the forms of thermometers and barometers, glass had also been a major contributor to the Scientific Revolution. In particular it led the antique *horror vacui* to be ruled out for good and measurements ranging from the springiness of gases to sap and blood pressure to be made. Finally, electricity also strongly relied on glass. When discovered, the two kinds of electricities were termed *vitreous* and *resinous* whereas glass found itself a critical component

of Leyden jars and electrostatic machines. In the second part of the 19th century, the problem of electrical conduction of rarefied gases in glass tubes finally leads to the discoveries of X-rays and the electron. Glass has thus been an irreplaceable agent of scientific inquiry through its unique combination of limitless shapability, transparency, optical isotropy, tightness to air, chemical inertness, wide compositional ranges, weldability with metals, and dielectric properties.

10.11. A History of glass science

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In terms of both products and processes, glassmaking has been a highly successful but purely empirical activity for more than three millennia. Natural philosophers did pay attention to glass in Antiquity, but their emphasis on its kinship with metals did not lead to any better fundamental understanding of its properties. Likewise, alchemy did not result in any advance despite the dual importance it attached to glass as a material and as an illustration of the deep transformations of matter that man could effect. In the 17th century, it was at the time of the Scientific Revolution that new concepts appeared. When van Helmont experimented with glass dissolution, Descartes gave the first description of vitrification at a microscopic scale while the possibility of achieving outstanding mechanical properties was announced by Prince Rupert's drops. From the late 18th century, the chemical revolution then led to the modern notion of chemical composition and to the discovery of the elements that make up glass (silicon, alkali and alkaline earth elements, etc.). Studies of glass crystallization and crystal melting gave a clearer picture of the mutual relationships of the two kinds of phases and, in particular, demonstrated the kinetic nature of the vitrification process. Following the discovery of a great many new elements, investigations were made from the mid 19th century to determine their glass-forming abilities and their effects on physical properties of practical interest. Particularly noteworthy outcomes of this work were the considerable diversification of optical glasses and the invention of the commercially important borosilicates. Systematic investigations of physical properties then began to be made as a function of composition and temperature. Whereas phase diagrams gave a sounder basis to glassmaking, tempered glass and Griffith's theory of rupture were important mechanical achievements. Surprisingly, however, the specificity of glass as a material was not understood until the 1920s when the

existence of a glass transition was at last recognized through calorimetric measurements. The issues of relaxation and viscoelasticity were then raised, benefitting much from the theoretical framework set earlier for mechanical systems displaying delayed responses. In the meantime, the random network model of glass structure had been formulated and the new technique of X-ray diffraction had been used for the first structural determinations, quickly followed by Raman spectroscopy. Glasses are now made in a variety of chemical systems and by other methods than melt quenching. Some of them are unstable at high temperatures before undergoing a glass transition. Although these features make a general statement difficult, one can define glass as a macroscopically homogeneous amorphous solid whose properties (physical, chemical, or structural) vary with its preparation conditions.

10.12. Glass Museums

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The current definition of a museum by the International Council of Museums is rather all-encompassing, and so are the many forms that a glass museum, or a glass collection within a museum, can take. Since the Middle Ages, perhaps even earlier, glass artefacts have been kept in (church) treasures, and the first deliberate and exclusive display of a glass collection seems to have taken place in 1713–1714, in the glass cabinet of Rosenborg castle in Copenhagen. Characteristic types of glass collections/museums are the princely collections, museums of decorative arts and of cultural history, archaeological collections, scientific and technical museums, as well as a variety of regional and other specializations. Most of these aspects are being addressed by The Corning Museum of Glass, the most comprehensive of the world. Glass museums are facing a number of challenges, such as the demand for a continuously growing number of visitors, but they can count on a material that has caught the curiosity and imagination of the people for millennia, and continues to provide a great technological challenge and potential.

11.1. Postface — A personal retrospective

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