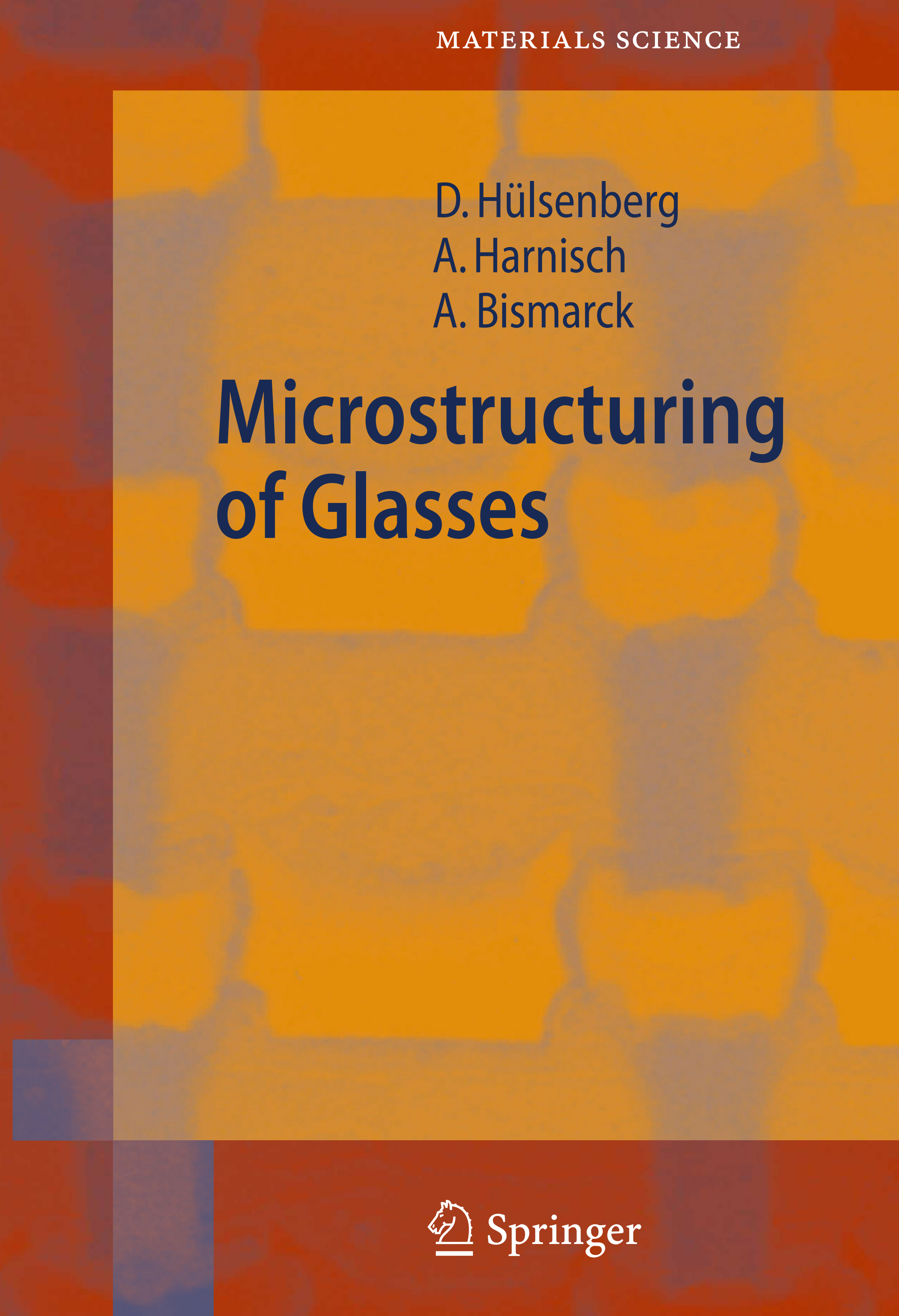

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Microstructuring of Glasses

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With 217 Figures

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Preface

Silicon, the second most abundant element on earth, is a well-established material in microsystems technology. Its properties and technical perfection open up an almost unlimited range of applications. Silicon is the main component of most semiconductor devices, but other materials are also applied step by step in microsystems technology so as to obtain some special properties. Glass is one such material that has some special properties.

Glass-making has a history of almost six millennia. However, the science of glass started only around 1830. But even by the end of the sixteenth century (or the beginning of the seventeenth century), glass articles were decorated with very fine gravured patterns in the form of meanders or garlands, combined with other bas-relieved decors [488]. Many of the patterns were made using copper wheels. Frequently the line width was less than 100 µm. Around 1920, glass-cutting tools positioned in pantographs were used for scratching fine lines into waxed surfaces of glass products. The lines were then transferred into the glass by hydrofluoric acid treatment, resulting in permanent patterns. These final patterns consist of lines that are 200 µm wide and deep. Till date, we find glassware such as drinking glasses and candlesticks being decorated using this technique. This method was also used to produce the scaling of clinical thermometers and laboratory glasses. Powder blasting for decorating glass products and treatment with a diamond tool for producing glass scales have been known for more than 50 years and remain the state of the art even today.

Between 1940 and 1950, Dalton, Armistead and Stookey, while working for Corning (USA), discovered that specially composed, UV-sensitive glasses can be micro ‘sculptured’. Partial UV exposure through a mask, followed by thermal and chemical treatments, allow for a defined microstructuring of glasses in a 10-µm range. Unnoticed by the world, the age of glass microstructuring had started, possibly 30 years too early. Only with the rise of silicon technology did microstructuring of glasses become important.

Glass is an amorphous material with a unique property profile. Glasses offer different transparency ‘windows’ for electromagnetic radiation, have superior chemical stability, are biocompatible, have excellent abrasion resistance and allow for adapting their thermal expansion coefficients to those of other materials. Glasses can be electrically insulating, but they can also be good ion conductors or even semiconductors. The properties of glasses depend strongly on the chemical composition of the glass itself, which can vary widely. The property profile opens a wide range of applications of different glasses in microtechnology. The amorphous character of glasses implies that all its properties are isotropic and that the ability of microstructuring is therefore independent on predefined directions of crystal lattices. Sometimes glasses are the only material that fulfil the specifications for special applications.

As a consequence, and in contrast to silicon, quite different glasses can be used for microstructuring. The producer of microdevices has to select a glass that is suitable for his application and also has a composition that offers the desired property profile. Mostly, the amount of glass ordered is relatively small. Of course, the glass industry is able to produce special glasses, but it is costly to produce very small quantities of glasses with specific composition. It is therefore a disadvantage for the glass producer if a customer demands very small quantities of a glass having a specific composition. For this reason, it would be good to have a theoretical idea of the feasibility of producing a desired glass in a certain small quantity.

Silica coatings, light wave guides, silicon sensor encapsulations and membranes in piezo-driven ink jet printers were the first applications of glass elements in microcomponents. The ability to fabricate extremely thin glass components without additional, geometrical structuring was the only requirement for these early applications. The need for small holes allowing for electrical connections through thin glass coatings to the silicon element soon required additional machining. Initially, these were manufactured by drilling. As of date, almost every geometrical feature that is needed at or near the surface and even in the bulk of the glass element can be made.

However, because of limited communication and knowledge transfer between the glass manufacturer and the microsystems industry, it is hard for the glass manufacturers to estimate the issues and the real demand for microstructured glasses in the microsystems area. Vice versa, the specialist in the microdevices industry cannot assess the full range of possibilities and problems of this amorphous, brittle material. The aim of this book is to link the thinking and understanding of specialists in terms of glass production as well as the fabrication of microdevices. The book attempts to explain the most important fundamentals, methods, features and highlights in the production of glass half products used for microstructuring as well as the microstructuring itself. It does not cover the entire subject matter, because of the growing nature of this field. Rather, the purpose of this book is to provide the newcomer to glasses with enough background to be able to access the specialist literature. Therefore, we start with the basics of glass materials and frequently refer to existing publications so that readers across cognate disciplines can easily understand what happens, for instance, between the ions in the glass and the ways in which glass processing affects the final properties of glass microdevices. The book's aim is to present an additional source of information on the three aspects, namely, the fundamentals of glass composition and glass processing and the many different methods of its microstructuring. It provides a comprehensive discussion of the various microstructuring methods, with appropriate references to literature, so that the book can be used as a source of information for glass manufacturers, producers of microdevices, engineering professionals with a background in designing (of microdevices) and structuring processes, as well as scientists in general, and students in particular.

The book is divided into two main parts:

Part I deals with the fundamentals of inorganic-nonmetallic glasses and their processing.

Part II explores and explains the principles of geometrical microstructuring of glasses, joining processes and applications.

First (Part I), an introduction to the amorphous state of glasses provides the background to the study of glasses, which is necessary for understanding the unique role of glass in microsystems. This is followed by a description of the characteristics and properties of specific glasses that are important for microsystems. The reader is then provided with information about glass processing, keeping in mind the requirements and specifications of microglass elements.

Part II provides the reader with a general overview of geometrical microstructuring and the special methods used for mechanical, thermal and chemical structuring of glasses. It focuses on methods of glass structuring, using various types of lasers, as well as on structuring of photosensitive glasses. The book also describes in some detail the methods of joining glasses with themselves as well as with other materials, such as silicon. The discussion of the methods is supplemented with relevant applications.

The book focuses mainly on subtractive methods, i.e. the removal of material, and on thermal reshaping methods as well as techniques that allow for the manipulation of locally confined properties. We do not discuss ion or electron beam structuring, because of their limited application in industry; nor do we discuss additive methods such as the deposition of powders or coatings. Silicate glasses form the centre of discussion of the book. We also exclude special microoptics and photonics made from glasses because excellent specialist books are already available, and the reader is referred to them; the processing associated with their manufacture is, however, described in different sections of the book.

We hope that the reader will find sufficient interesting facts and be motivated to use glasses for microdevices. We welcome comments to this work.

Ilmenau, Langewiesen, London,
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List of abbreviations

Symbol	Description	Unit
α	Thermal expansion coefficient	$10^{-6}\,\mathrm{K}^{-1}$
α_i	Thermal expansion coefficient of the ith component	$10^{-6}\,\mathrm{K}^{-1}$
β	Angle of inclination	°
β	Composition dependent materials transition number	$\mathrm{g\ cm^{-2}\,s^{-1}}$
β_E	Absorption coefficient	mm^{-1}
β'_E	Non linear absorption coefficient	mm^{-1}
γ	Surface tension	$\mathrm{N\ m^{-1}}$
$\dot{\gamma}$	Shear rate	s^{-1}
$\mathit{\Delta}$	Loss angle, phase displacement between current and voltage	°
$\mathit{\Delta}_\mathrm{b}H^\circ$	Standard enthalpy of formation	$\mathrm{kJ\ mol^{-1}}$
$\Delta_\mathrm{b}S^\circ$	Standard entropy of formation	$\mathrm{kJ\ mol^{-1}\,K^{-1}}$
$\Delta\mathrm{bg}$	Widening of trenches/holes	µm
$\Delta\mathrm{bs}$	Reduce of width of beams/bars	µm
Δc	Concentration gradient	–
Δg_V	Change of the free volume enthalpy during nucleation	$\mathrm{kJ\ mol^{-1}}$
Δo.D.	Difference of the optical density	–
ΔT	Super or under cooling	°C
ε	Strain	%
ε_Ab	Threshold energy density for ablation	$\mathrm{J\ cm^{-2}}$
ε_L	Laser beam intensity, energy density of laser irradiation	$\mathrm{J\ cm^{-2}}$
ε_O	Electrical field constant	$\mathrm{As\ V^{-1}m^{-1}}$
ε_S	Threshold energy density for photo chemical effects	$\mathrm{J\ cm^{-2}}$

η	Dynamic viscosity	Pa s^{-1}, dPa s^{-1}
κ	Specific electrical conductivity	Ω^{-1} cm^{-1}
λ	Heat of two-dimensional condensation	J
λ	Shear deformation rate	–
λ	Thermal conductivity	W m^{-1} K^{-1}
λ	Wavelength	µm, nm
λ_L	Laser wavelength	nm
ρ	Specific electrical resistivity	Ω cm
ρ	Density	g cm^{-3}
σ	Interfacial tension	N m^{-1}
σ	Normal stress or strength	MPa
σ_B	Bending strength	MPa, MN m^{-2}
σ_f	Failure strength	N mm^{-2}
σ_m	Theoretical stress	N mm^{-2}
σ_y	Yield stress	MPa
σ_z	Tensile strength	MPa, MN m^{-2}
τ	Optical transmission	%
τ	Shear stress	Pa, MPa
χ	Susceptibility	–
ω	Angular frequency	s^{-1}
A	Area, surface area	cm^2
A	Aspect ratio	–
A_E	Optical absorption	–
A_R	Fracture area	mm^2
A_{US}	Ultrasonic amplitude	µm
a	Half flaw length	nm
B	Magnetic field, magnetical flux density	T, Wb m^{-2}
B	Chemical binding energy	J mol^{-1}
bg_i	Real width of trenches/holes (after thermal treatment and etching)	µm
bg_s	Nominal width of trenches/holes	µm
b_s	Distance between crossing perforations	µm
bs_i	Real width of bars/beams (after thermal treatment and etching)	µm
bs_s	Nominal width of beams	µm
C_p	Specific heat capacity	J K^{-1} mol^{-1}
c	Concentration	–
c	Speed of light	km s^{-1}
c_{Ag}	Concentration of silver ions	%
D	Deformation rate, shearing rate	s^{-1}
D	Energy density	J cm^{-2}
D	Diffusion coefficient	cm^2 s^{-1}

D	Energy to dissociate oxides	J mol^{-1}
D_{min}	Minimum density of energy	J cm^{-2}
D_{s}	Relative resp. normalized density of energy	–
d	Machining depth, thickness, crystal size	µm
d_{50}	Grain size of particles: 50% are smaller and 50% greater than this value	µm
d_{C}	Critical tension depth	µm
E	Young's modulus	GPa
E_{η}	Activation energy for viscous flow	kJ mol^{-1}
E_{B}	Energy of binding, effective band gap	eV
E_{D}	Activation energy for diffusion	kJ mol^{-1}
E_{E}	Enthalpy of evaporation	kJ mol^{-1}
E_{P}	Energy for ductile deformation	J
E_{Ph}	Energy of a photon	eV
E_{R}	Energy for generation of new fracture surfaces	J
F	Area	cm^{2}
F	Force	N
F_{E}	Electrical Field strength	V m^{-1}
$\vec{f}_{\mathrm{L,e}}$	Lorentz force density, externally caused	N m^{-3}
G	Shear modulus	GPa
G	Free (or Gibbs) enthalpy	J mol^{-1}
G	Griffith crack propagation parameter	N mm^{-1}
G^{*}	Activation energy for nucleation	kJ mol^{-1}
G_{v}	Free volume enthalpy	kJ mol^{-1}
G_{O}	Free surface enthalpy	kJ mol^{-1}
g	Acceleration due to gravity	m s^{-2}
g	Width of not transparent lines	µm
H	Enthalpy	kJ mol^{-1}
H	Hardness	MN m^{-2}
h	Depth of structures (after etching) or of bottom topography (roughness)	µm
h_{c}	Cutting speed, speed of the tool	µm s^{-1}
h_{d}	Depth of diffusion	µm
h_{f}	Feed rate	mm min^{-1}
h_{f}	Depth of relicts	µm
h_{k}	Crystallisation depth	µm
I	Intensity of irradiation	W cm^{-2}
I_{0}	Initial light intensity	W cm^{-2}
i	ith component	–

i	Distance between the median lines of two absorber stripes or transparent perforations, period	µm
i	Imaginary unit	–
J_n	Relative intensity	–
J_E	Electrode current	A
$J_{\mathrm{n\ h=1}}$	Relative depth intensity (depth of 1 mm)	–
J_nges	Relative total intensity	–
J_nges/h	Depth related, relative total intensity	mm^{-1}
$J(T)$	Rate of nucleation (including diffusion processes)	s^{-1}
j	Particle current of diffusing particles from a given volume through an area	$\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$
$\vec{j}$	Electric current density	$\mathrm{A\ cm}^{-2}$
K_IC	Critical fracture toughness	$\mathrm{MPa\ m}^{1/2}$, $\mathrm{MN\ m}^{-3/2}$
KG	Rate of crystal growth	$\mathrm{µm\ min}^{-1}$
k	Boltzmann constant	$\mathrm{J\ K}^{-1}\,\mathrm{atom}^{-1}$
M	Molecular weight	$\mathrm{g\ mol}^{-1}$
m	Mass	g
$\dot{m}$	mass flow	$\mathrm{g\ s}^{-1}$
m_i	Content of the ith component	–
N	Rate of nucleation without considering the diffusion	$\mathrm{s}^{-1}\,\mathrm{cm}^{-3}$
N	Number of species	–
N	Number of pulses	–
N_eff	Effective number of pulses	–
n	Number of components	–
n	Refractive index	–
n'	Nonlinear refractive index	–
n_0	Refractive index for isotropic materials and linear polarized light	–
n_1	Refraction constant	–
n_2	Absorption constant	–
n_s	Spindle frequency	rpm
o	Width of transparent perforations	µm
o/g	Line ratio, perforation ratio	–
P	Power density	$\mathrm{W\ cm}^{-2}$
P	Tensile force	N, MN
P_E	Polarization	$\mathrm{C\ m}^{-2}$
p	Pressure	MPa
Q	Ratio of etching	–
R	Gas constant	$\mathrm{J\ K}^{-1}\,\mathrm{mol}^{-1}$
Ra	Arithmetic mean roughness	nm, µm

R_E	Reflection	–
Rz	Surface roughness	nm, µm
r	Radius	mm
r	Griffith flaws radius	nm
r	Nucleus' radius	nm
r_o	Characteristic ion distance	nm
r^*	Critical nucleus' radius	nm
S	Entropy	J mol^{-1} K^{-1}
s	Proximity space, displacement, deflection	µm, mm
T	Temperature	K, °C
T_0	Equilibrium temperature	K
T_g	Transformation temperature	°C
$T_{\kappa\ 100}$	Temperature of a material with $\rho = 10^8\ \Omega$ cm	°C
T_liqu	Liquidus temperature	°C
T_melt	Melting temperature	°C
T_sinter	Sintering temperature	°C
T_O	Annealing point	°C
T_R	Room temperature	°C
T_U	Strain point	°C
TA	Ratio of transmission	–
t	Time	s
t	Duration of a laser pulse	fs
t_d	Time of diffusion	h
t_e	Time of etching	s, min
t_L	Exposure time	s, min
U	Internal energy	J · mol^{-1}
V	Deformation	%
V	Volume	cm^3
V	Specific volume	cm^3 g^{-1}
V_M	Molar volume	cm^3 mol^{-1}
$V_\mathrm{M,\ eff}$	Effective molar volume	cm^3 mol^{-1}
V_P	Plastically deformed volume	mm^3
v_b	Rate of bubble rising	m h^{-1}
v_c	Cutting rate, speed of the tool	m s^{-1}
v_e	Etching rate	µm min^{-1}
v_f	Feed rate	mm s^{-1}, mm min^{-1}
x,y,z	Geometrical coordinates	mm
z	Depth	mm
z	Valence number	–
BHF	Barium hexaferrite	
cw	Continuous wave	
Cps	Counts per second	

CN	Coordination number	
CPM	Colliding pulse mode	
CTE	Coefficient of thermal expansion	
CVD	Chemical vapour deposition	
DC	Direct current	
DIN	Deutsche Industrienorm (in German)	
DNA	Deoxyribonucleid acid	
DSC	Difference scanning calorimetry	
DTA	Difference thermo analysis	
DUV	Deep ultra violet	
EUV	Extrem ultra violet	
HF	Hydrofluoric acid	
HPSN	Hot pressed silicon nitride	
IR	Infrared radiation	
LCD	Liquid crystal display	
LIGA	Lithographie, Galvanoformung, Abformung (in German)	
LMS	Lithium meta silicate	
MEMS	Microelectromechanical systems	
NC	Numeric control	
NIR	Near infrared	
o. D.	Optical density	
PMMA	Polymethylmethacrylate (Perspex)	
PVD	Physical vapour deposition	
RF	Radio frequency	
SAE	Spin agitated etching	
SEM	Scanning electron microscope	
SiSiC	Silicon infiltrated silicon carbide	
TFT	Thin film transistor	
UV	Ultraviolet radiation	
VAD	Vapour axial deposition	
VIS	Visible radiation	
XRD	Röntgen diffractogram, X-ray diffraction	

Part I

Fundamentals of Inorganic Nonmetallic Glasses and Glass Processing

1

Silicate Glasses: A Class of Amorphous Materials

1.1 Structure of Glasses: Ionic Arrangement

1.1.1 Preliminary Remarks

The understanding of the technical processes of geometrical microstructuring of glass components presumes the knowledge of the materials structure, i.e. their microstructure as well as the arrangement of and the interaction between the ions. It is necessary to distinguish between the materials microstructure and the aim of the process to create geometrically defined microstructures in glass components. Chapter 1 addresses the ionic and atomic arrangement in silicate glasses and its effect on the glass properties. The chapter is not exhaustive but explores the areas relevant to geometrical microstructuring.

As we see, the similarity of the terms *materials microstructure* and *geometrical microstructuring of components* signals the practical difficulty to separate them. The better we understand the behaviour of ions in glass, the better equipped we are to technically influence geometrical microstructures in glass components. We will use accessible language to explain the solid-state fundamentals and chemical processes, so that, for example, specialists working in mechatronics can use the book as quick and practical reference.

Concerning the properties of silicate glasses it is very interesting that they are extremely brittle materials but if used in fibre form in reinforced polymers, they provide the composite with strength. It is well known that the smaller the diameter of the glass fibres, the higher their strength. It can be expected that small microstructured glass components with the desired property profile of interest for applications in microtechniques can be produced.

1.1.2 Coordination Polyhedra

Silicates are salts of silicic acids and contain in each case SiO_2. Silica or quartz glass contains only SiO_2. All other glasses used for geometrical microstructuring contain also other oxides, such as Li_2O, Na_2O, K_2O, MgO, CaO, BaO,

B_2O_3, Al_2O_3, etc. The principle of electroneutrality governs in the smallest space [225], i.e. the charge of cations is compensated by anions. This can only be achieved if the anions directly surround the cations and screen their charge by their volume and charge and vice versa. The consequence of these geometric requirements is the coordination polyhedra and their 3D network in solid silicate glasses.

The coordination number *CN* defines the number of ions X (in this case O^{2-}) that surround a central ion A (here $Li^+ \ldots Mg^{2+} \ldots B^{3+} \ldots Si^{4+} \ldots$) in the same distance. Provided that the ions can be considered as hard spheres coordination numbers from 3 to 12 can be found in silicate glasses [225]. Figure 1.1 shows schematically all possible geometrical configurations. *CN* depends on the charge and the radius of the individual ions. Furthermore the deformability especially of the anions and the larger cations should be taken into account [475]. Figure 1.2 shows polyhedra which are common for silicate glasses [439]. Figure 1.2 (left) shows an isolated SiO_4-tetrahedron, however the schematic does not show the nominal negative charges of oxygen ions. The oxygen is bonded to the silicon in the centre of one tetrahedron and to another silicon from a neighbouring but, not shown, surrounding polyhedron. In case of the ${MgO_6}^{10-}$ octahedron (right-hand side of Fig. 1.2) each of the O^{2-}-ions obtains nominally 1/3 electron from the central Mg^{2+}-cation and 5/3 electrons from the neighbouring octahedra. To compensate the charge fully, if only Mg^{2+}-cations are present, five such additional ions are necessary. *CN* of oxygen by only magnesium in the neighbourhood is 6. However, if the glass contains different types of cations, they all screen the charge of the oxygen. In this case it is rather complicated to determine *CN* for oxygen, because the distance between oxygen and the various surrounding cations varies so that the precondition for the determination of *CN* is not fulfilled. Therefore, it is not common to provide *CN* for oxygen in glass.

Regardless of glass type short- and long-range ordering of the ions has to be distinguished. The coordination polyhedra represent the short-range order of the glass. They exist in silicate glasses whether or not they are in the melt or solidified (glass) state. The long-range order characterises the periodicity or repetition of distances and angles of neighbouring polyhedra, which provides the basis for a regular lattice in crystals. However, a perfectly homogeneous glass does not possess any long-range periodical order. The absence of any long-range ordering is essential for the amorphous state. Transitions in glass between short-range ordering and emerging long-range ordering will be discussed in Sect. 1.1.4.

1.1.3 Dominating Role of Silica Tetrahedra in Silicate Glasses

In order to understand the role and importance of silica tetrahedra in glass, we should revisit a silicon atom. Silicon contains 14 electrons, which occupy different energy levels or orbitals. The state of an electron in an orbital is given by its four quantum numbers; the primary, azimuthal, magnetic and

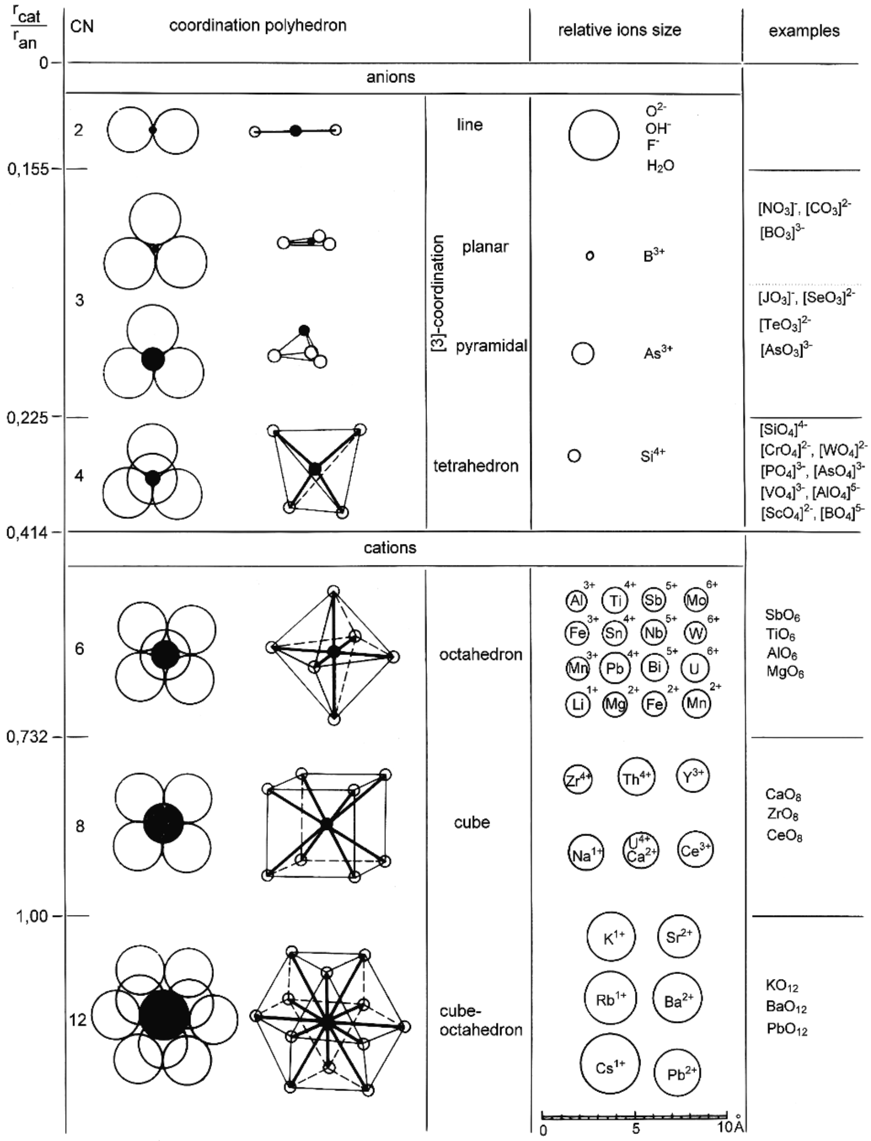


Fig. 1.1. Various coordination polyhedra depending on the ratio of the cation to the anion size and their charge [225]

spin quantum number. Only a small amount of energy is required to transfer an electron from an energy level to another. The valence electrons, i.e. those that occupy the outermost electron orbitals, are those that undergo chemical reactions. Only a small amount of energy is sufficient to rearrange the electrons in the outer orbital, to change especially the azimuthal and spin quantum

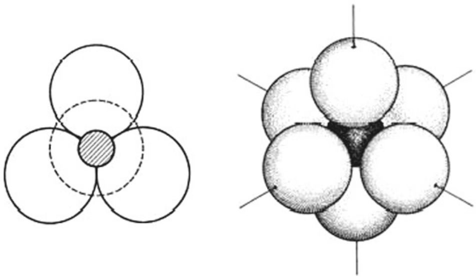


Fig. 1.2. Isolated silica-tetrahedron, (*left*) and MgO_6-octahedron, (*right*)

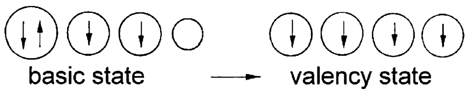


Fig. 1.3. The valence electrons of the silicon atom in the fundamental (*left*) and in the excited (*right*) state [538]

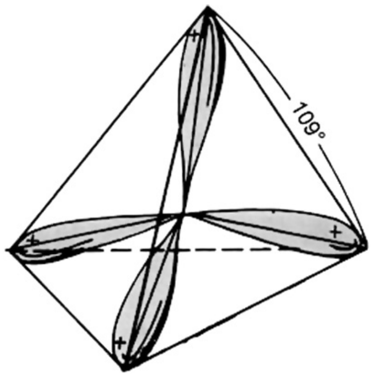


Fig. 1.4. sp^3-hybrid orbitals of silicon [225]

numbers. A hybridisation process takes place; atomic orbitals form hybrid orbitals [398]. All electrons in the highest energy level of silicon obtain a parallel spin moment, and the electrons in the s-orbital with an antiparallel spin quantum hybridise with the p-electrons to form sp^3 orbitals. All valence electrons occupy hybrid orbitals with equal energy and have parallel spins (see Fig. 1.3). Figure 1.4 shows the excited state of the silicon atom.

These sp^3-electrons are magnetically equivalent. It follows that the excited state is not stable, so that the sphere like outer shell of the atom deforms into a tetrahedron with the valence electrons in the four corners. The four excited electrons turn towards the energy donors for other molecules, which are in our case oxygen molecules, possessing potential and kinetic energy. The homopolar bonding of the O_2-molecules is dissolved, and four oxygen

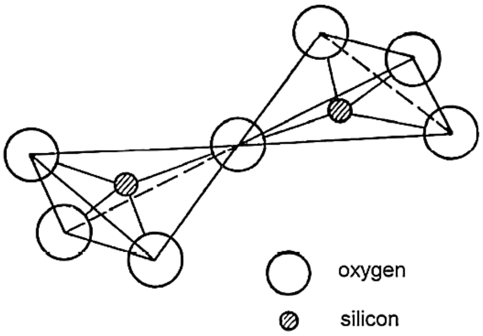


Fig. 1.5. Knotting together of two silica tetrahedra by a bridging oxygen

atoms are fixed to the electrons in the four corners of the former silicon atom (Fig. 1.2, left). Each oxygen atom receives formally one electron, and Si^0 converts into Si^{4+}, see once more Fig. 1.4. However, oxygen anions require two electrons to achieve a stable noble gas configuration. They obtain the second electron from neighbouring silicon ions, which are from themselves the centre of another ${SiO_4}^{4-}$-tetrahedron, and the oxygen forms a bridge between two tetrahedra (see Fig. 1.5).

The bridging oxygens join the corners of neighbouring tetrahedra. The Si–O–Si bond angle could become 180°, which however is an exception. Usually the bond angle varies in wide limits and is not constant in glasses, which hinders any long-range ordering. In contrast to the bridging Si–O–Si bond angle, the O–Si–O bond angle at the centre of the tetrahedron is always constant at $109^\circ\ 28'$, which highlights the short-range order between the associated ions (Fig. 1.4).

Silica tetrahedra are extremely stable. We will only briefly explain this fact. For a detailed explanation please refer to specialist glass materials books, such as Hinz [225], Scholze [449, 450] and Vogel [538].

In order to explain the stability of the silica (${SiO_4}^{4-}$) tetrahedron we have to consider the electronegativity of ions as defined by Pauling [398] (Fig. 1.6). A large difference in the electronegativity of two ions would lead to a predominately heteropolar bond between the ions, which would suggest that in ${SiO_4}^{4-}$-tetrahedra heteropolar binding dominates. However, recall the hybridisation of the valence electrons in silicon, which contributes a considerable homopolar character to the bond. Therefore, a mixed binding results in and between ${SiO_4}^{4-}$-tetrahedra.

The enormous stability of ${SiO_4}^{4-}$-tetrahedra can also be explained in terms of the radius of the ions and their electrical charge, i.e. the electrical field strength of the ions. Table 1.1 provides an overview of some ions radii of interest for silicate glasses. The radii of Si^{4+} and O^{2-} are very different.

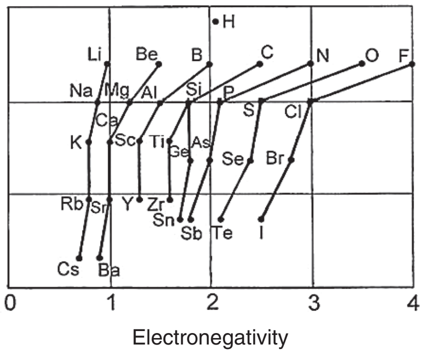


Fig. 1.6. Connection between the electronegativity of the ions and their position in the periodic table of elements [398]

Table 1.1. Radius (nm) of ions important for silicate glasses [224]

I	II	III	IV	Odd series	VI	VII
Li^+	Be^{2+}	B^{3+}	Si^{4+}	Fe^{2+}	O^{2-}	F^-
0.068	0.035	0.023	0.042	0.074	0.132	0.133
Na^+	Mg^{2+}	Al^{3+}	Sn^{2+}	Fe^{3+}	S^{2-}	Cl^-
0.097	0.066	0.051	0.092	0.064	0.174	0.181
K^+	Ca^{2+}	–	Sn^{4+}	Cr^{3+}	–	–
0.133	0.099		0.071	0.063		
Rb^+	Sr^{2+}	–	Pb^{2+}	Zn^{2+}	–	–
0.147	0.112		0.120	0.074		
Cs^+	Ba^{2+}	–	Pb^{4+}	Zr^{4+}	–	–
0.167	0.134		0.084	0.079		
–	–	–	–	Ti^{4+}	–	–
				0.068		

The electrical field strength F_{E} is proportional to the valence number z and inversely proportional to the square of the ion radius r (1.1):

$$F \sim \frac{z}{r^2}, \tag{1.1}$$

which explains the strong attractive interaction of Si^{4+} to O^{2-}.

The O^{2-} in the silica tetrahedron did acquire two electrons to establish a stable noble gas configuration, but the additional electrons enhance the repulsive interaction in the outer oxygen shell so it becomes more deformable. As a consequence, the Si^{4+}-cation in the centre of the tetrahedron deforms the O^{2-}-anions. The O^{2-}-anion is deformed by the Si^{4+}-cation like a dented rubber ball. That this fact is correct, one can see in Fig. 1.7. The distance between the nuclei of Si^{4+} and O^{2-} is not equal to the sum of the ions radii ($r_{\mathrm{Si}^{4+}} + r_{\mathrm{O}^{2-}} = 0.042\,\mathrm{nm} + 0.132\,\mathrm{nm} = 0.174\,\mathrm{nm}$, see Table 1.1), but

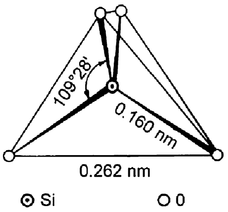


Fig. 1.7. Silica-tetrahedron containing the characteristic bond length and angles [225]

is smaller: 0.160 nm, which confirms that O^{2-} is deformed in the direction to both neighbouring tetrahedra. The bond is almost not polarised. Only the bridging oxygens show this peculiarity. The deformation of the O^{2-} has a further consequence. The four anions screen the Si^{4+}-cation completely so no interaction between the Si^{4+}-centres of neighbouring polyhedra takes place. All these facts explain the extraordinary stability of the silica-tetrahedron.

The silica tetrahedra are linked via bridging oxygen at all four corners, which results in the formation of 3D network of silica tetrahedra. Because of the distribution of the bridging oxygen (Si–O–Si) bond angles this 3D network structure is relatively disordered. As a result of which three, four or even more tetrahedra form hollow rings with interstices of various sizes and shapes in their centre (Fig. 1.8). The shape of the network rings is spherically deformed, and furthermore the number of silica tetrahedra in these rings varies. In order to visualise the 3D network of silica tetrahedra binding in a 2D form, the fourth bridging oxygen anion has to be neglected. A simplified model of a pure silica glass is shown in Fig. 1.8. The fourth bridging oxygen would stick out above and below the paper plane. Figure 1.8 provides a first imagination of the ionic microstructure of silica glass.

Most silicate glasses consist not only of silica, but also many other oxides. Only Ge^{4+}, P^{5+}, and under special circumstances also Al^{3+} and B^{3+}, are surrounded by four oxygens. They occur in the coordination number 4. These cations can substitute Si^{4+} in the tetrahedron. The bond between Ge^{4+} and O^{2-} is not as strong as in case of the Si^{4+}, because of the bigger radius of Ge^{4+}-ions. It is obvious that if B^{3+}, Al^{3+} and P^{5+} substitute Si^{4+} in the tetrahedra the resulting tetrahedra are more or less negatively charged and are therefore not in relating to space equilibrium. The missing or added (compared with Si^{4+}) positive charge has to be compensated. Additional monovalent cations are able to compensate the missing positive charge; P^{5+}-tetrahedra exhibit a double binding. Therefore the tetrahedra are not symmetrical, and this substitution of silica by other oxides reduces the stability of the resulting tetrahedra. Also in these cases the tetrahedra form 3D networks through bridging oxygen. ${BO_4}^{5-}$ (together with ${BO_3}^{3-}$), ${SiO_4}^{4-}$-, ${GeO_4}^{4-}$- and ${PO_4}^{3-}$-tetrahedra can form glasses on their own. Therefore, these oxides are called network formers. The more network former oxides a glass contains the more stable is the

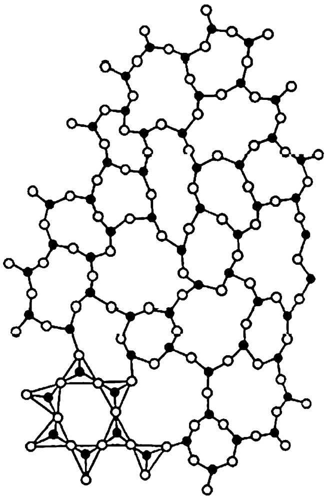
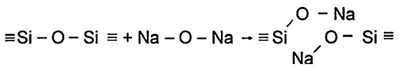


Fig. 1.8. Schematic 2D representation of a network of silica tetrahedra in a pure silica or quartz glass. A fourth bridging oxygen would be located directly below or above the silica [546, 574]



$$\equiv\text{Si}-\text{O}-\text{Si}\equiv+\text{Na}-\text{O}-\text{Na}\rightarrow\equiv\overset{\diagup\text{O}-\text{Na}}{\text{Si}}\quad\underset{\text{Na}\diagup}{}\text{O}-\text{Si}\equiv$$

Fig. 1.9. Very simplified model of the effect of the network modifier Na_2O

glass; i.e. the higher its melting temperature, its electrical resistivity and its chemical stability.

If bridging oxygens exist, so must be nonbridging oxygens, but how do they form? Any other cations as the few mentioned above are, if present in a glass, surrounded by more than four oxygens, it could be six, eight or even twelve oxygens. These cations require, in order to obtain charge neutrality (screening), more surrounding oxygens in the glassy network as compared to network former cations. The bond between a cation and oxygen becomes more heteropolar, if the distance between the cation and oxygen increases. This fact is easily explained if monovalent alkaline ions are present in a glass. These ions interrupt the oxygen bridge Si–O–Si, which leads if added Na_2O to the formation of two nonbridging oxygens (Fig. 1.9). In order to maintain charge neutrality of the glass each nonbridging oxygen formed must be linked to a Si^{4+}-ion and an additional cation in its surrounding.

Oxides which decrease the connectivity of the glassy network are called network modifier. The higher the amount of network modifiers in a glass formation, the higher the concentration of nonbridging oxygens. The formation of nonbridging oxygens causes the disruption of the direct connection between the tetrahedra, which results in the drastic reduction of the melting

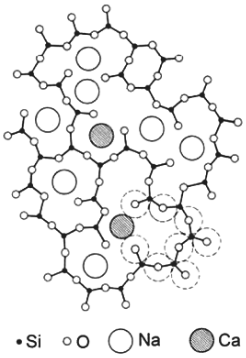


Fig. 1.10. A 2D representation of the structure of a soda lime silicate glass. A fourth bridging oxygen would be located directly below or above the silica [449]

temperature, melt viscosity, chemical stability, electrical resistivity but causes an increase of the thermal expansion coefficient.

Alkaline and alkaline earth oxides are effective network modifiers. The cations Na^+ and Ca^{2+} are usually associated to six or even eight oxygens to achieve charge neutrality. Therefore, they are positioned inside the interstices formed by the network former tetrahedra near the disrupted oxygen bridges (Fig. 1.10).

The free unoccupied volume in the interstices formed by the connected network former oxide tetrahedra determines the basic volume and, therefore, the density of the glass. Any network modifiers that will occupy the empty interstices will lead to an increase of the density of the glasses. The density increase depends of course on the atomic mass and the concentration of the modifier cations within the glass. However, it is not unlimited. The limit depends on the size of the interstices as well as the radius of the network modifier cations. If the network modifier cations are large it will cause the original network to expand, i.e. the volume increases.

If these simplified principles of the ionic arrangement in glasses are understood, also people who do not possess any prior knowledge in glass materials will be able to follow the interrelation between the materials composition and properties of glasses, which is of great importance in connection to geometrical microstructuring of glasses.

1.1.4 Glasses as Supercooled Solidified Melts

Glass melts are liquids. Liquids are characterised by the absence of any long-range order. In liquids consisting of ions the principle of electroneutrality dictates that charge compensation has to take place with the consequence that polyhedra form. The stability of the polyhedra depends on the criteria described in Sect. 1.1.3. Silica tetrahedra are the most stable polyhedra in the melt. The geometrically bulky configuration limits their mobility. In contrast to bulky tetrahedra, heteropolar bonded alkaline and alkaline earth cations have a relatively high mobility in the melt. These cations often change their position in the different tetrahedron rings. As a consequence, the viscosity of glass melts therefore not only depends on the temperature but, at a given temperature, also depends on the relative concentration of network formers to modifiers and their exact composition. The dynamic viscosity of a glass melt is very high. Commonly processed glass melts have a dynamic viscosity of about 1–10 Pa s at the practical melting temperature. The geometrical shape of the silica tetrahedra causes the high melt viscosity of glasses and makes it impossible for the silica tetrahedra to assume by diffusion or by flowing a minimum energy equilibrium position, i.e. an imaginary lattice place of hypothetical crystals.

During the cooling process the viscosity of the glass melt increases continuously and so the possibility of tetrahedra or single ions to find hypothetical lattice places becomes even less likely. Crystallisation is completely made impossible if the glass melt solidifies. The result is a supercooled solidified melt, which means an amorphous glass. The estimated viscosity of a glass at room temperature is about 10^{18} Pa s. At low temperatures the brittle–elastic behaviour of glasses prevails. The complete dependence of the viscosity on temperature for a given glass is shown in Fig. 1.11. This curve is generally observed for glasses, but for a given glass composition the absolute position of the temperature axis of the viscosity–temperature graph strongly depends on the concentration ratio of network former to network modifier oxides. The more network former oxides, especially SiO_2, the glass contains the more this curve is shifted to higher temperatures. The slope of the curve depends on the amount and the type of network modifiers present. The more steep the

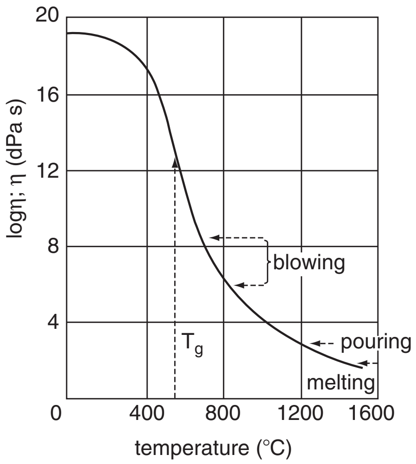


Fig. 1.11. Viscosity as function of temperature for a real soda lime silicate glass with the following composition (mass%): 71.7 SiO_2; 0.1 TiO_2; 1.2 Al_2O_3; 0.2 Fe_2O_3; 6.8 CaO; 4.2 MgO; 15.0 Na_2O; 0.4 K_2O and 0.4 SO_3 [449]

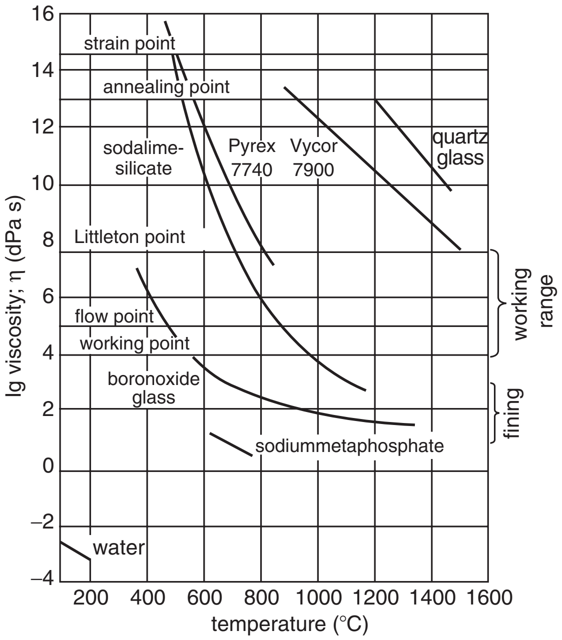


Fig. 1.12. Comparison of viscosity as function of temperature for various traditional glasses of interest to microstructuring [333]

slope of the viscosity–temperature curve, the more CaO the glass contains. An increasing Na_2O causes the curve to flatten. Of course the full explanation of the viscosity behaviour of glass melts is much more complex [420,422,535], but for the first interpretation of viscosity–temperature curves these simple rules might suffice. Figure 1.12 demonstrates the effect of the chemical composition of various glasses on viscosity–temperature curves. All types of glasses, such as alkaline alkaline earth silicate glasses, alkaline-alumino-silicate glasses, borosilicate glasses and pure silica glass are of equal interest for microtechnique applications.

Tailoring the viscosity–temperature behaviour of glasses is of special interest for all technical processes starting with melting, forming, cooling to the preparation of half products and even for geometrical microstructuring. Glass melts are usually processed at viscosities $\eta \approx 10^1$ Pa s. It depends on the necessary temperature of the melt if this processing step is technically challenging and expensive or not. Fining (see Sect. 3.3.1) and homogenisation (see Sect. 3.3.2) of the glass takes place in the melt. Both process steps are responsible for the materials microstructure. Geometrical microstructures in the glass can never be better than the materials microstructure.

Forming follows melt processing. Glasses can be formed by pouring. The melt viscosity during this process should be in the order of $\eta \approx 10^2$ Pa s. Other forming processes such as pressing, rolling, drawing and blowing require melt viscosities in the range of 10^3 Pa s $< \eta <$ $10^{6.6}$ Pa s (Fig. 1.11). The temperature belonging to a viscosity of 10^3 Pa s corresponds to the working point. Further hot-forming of glass half products by pressing, drawing etc. often takes place at a viscosity of $\eta \approx 10^5$ Pa s, but sometimes also at viscosities higher than $\eta \approx 10^{6.6}$ Pa s.

Cooling of the glass product follows the forming process. At viscosities lower than $\eta \approx 10^{12}$ Pa s, i.e. at relatively high temperatures, the glass can still undergo viscous flow. This fact prevents that temperature gradients could cause stresses. They will be immediately dissipated due to viscous flowing. The dissipation rate depends on the temperature. Formed glass products can be cooled down more rapidly at higher temperatures, but have to be cooled slower at lower temperatures. Problems begin to arise at viscosities $\eta > 10^{12}$ Pa s. Because of the reduced mobility of the silica tetrahedra, the glass melts ability for viscous flow decreases rapidly. The brittle–elastic behaviour increases accordingly. The transformation from a viscous glass melt to brittle–elastic behaviour will take place in the viscosity range 10^{12} Pa s $< \eta <$ $10^{13.5}$ Pa s. In this viscosity region the glass behaves as a visco–elastic solid. Both mechanisms overlap. The viscous behaviour is described by Newton's law (1.2), whereas the elastic behaviour by Hooke's law (1.3).

$$\tau = \eta(T)\ D \tag{1.2}$$

$$\sigma = E(T)\ \varepsilon \tag{1.3}$$

τ = shear stress
$\eta(T)$ = coefficient of dynamic viscosity
T = temperature
D = linear shear rate
σ = normal stress
$E(T)$ = elastic modulus
ε = strain

The visco-elastic behaviour of glasses can be described by Maxwell's law (1.4) [383]:

$$\dot{\gamma} = \frac{\tau}{\eta\,(T)} + \frac{\dot{\tau}}{G\,(T)} \tag{1.4}$$

$\dot{\gamma}$ = shear rate of an angle γ
G = shear modulus

From (1.4) follows that the dominating deformation mechanism depends on $\eta(T)$ and $G(T)$. It is also clear that a glass at any temperature has always a viscous and elastic contribution to its deformation behaviour. From this follows:

- At viscosities exceeding $\eta = 10^{12}$ Pa s, the rate at which stresses in glass products dissipate due to viscous flow reduces. Therefore in order to avoid the formation of residual stresses the cooling rate has to be reduced. The best option to produce stress-free glasses is to anneal the glass at temperatures in the transformation range 10^{12} Pa s $< \eta < 10^{13.5}$ Pa s. Viscous flowing becomes negligible if the glass melt is cooled below the strain point T_U at $\eta = 10^{13.5}$ Pa s. Therefore we repeat: Careful cooling in the transformation range is the best precondition to produce stress-free glass products.

- This transformation range has also direct consequences for glass microstructuring. During heating a glass starts to flow at the just called strain point. Microstructured glass components cannot be used at $T > T_\mathrm{U}$. Geometrical structures in the micrometer range would deform.

Most publications concerning glasses, but especially prospects of glass producers, do not publish T_U but prefer the glass transition or transformation temperature, T_g. T_g characterises the transformation range in general and is defined as the temperature at which a glass has a viscosity of $\eta = 10^{12.3}$ Pa s.

At all temperatures $T_\mathrm{liqu.} > T > T_\mathrm{g}$ the melt is a supercooled liquid. Its viscosity increases with decreasing temperatures. In the transformation range the melt becomes a supercooled, *solidified* glass with an amorphous structure.

1.1.5 Density of the Glass Network

Section 1.1.3 describes the arrangement of silica tetrahedra within a glass. Silica tetrahedra are linked at all four corners and form more or less deformed and disconnected rings of 3–12 tetrahedra, which have interstices of various sizes in the centre of the rings. Small network modifier cations, such as Li^+ and Mg^{2+}, are in principle able to occupy nearly all large and also small interstices in the network and thereby reduce the unoccupied (interstitial or free) volume. However, the larger the cation radius (see Table 1.1) the more difficult it becomes to fill all interstices. As a consequence larger ions tend to occupy only the interstices in large tetrahedron rings. The interstices in small rings could be left unoccupied if a glass contents only big network modifier cations. If a glass consists only of small ${\mathrm{SiO}_4}^{4-}$ tetrahedron rings and large network modifier cations, the glass network would have to expand during melting to accommodate the cations. It follows that the measured density of glasses strongly depends on the amount of network modifiers, their atomic weight and their ionic radius.

Glasses are more commonly characterised by measuring the specific volume V rather than the density $\rho(\mathrm{g\ cm^{-3}})$. The molar volume V_M, which is defined as the volume occupied by one mole of a glass, is obtained by dividing the materials molecular weight by its density (1.6):

$$V_\mathrm{M} = \tfrac{M}{\rho}\ [\mathrm{cm^3\ mol^{-1}}] \tag{1.5}$$

$$M = \text{molecular weight } [\mathrm{g\ mol^{-1}}]. \tag{1.6}$$

V_M includes the entire free volume of a glass, including the volume of the interstices. Therefore, it is larger than the sum of the volume occupied by all different cations and the oxygen. Assuming that ions are hard spheres, Hecht-Mijic [201] has defined an effective molar volume $V_{\mathrm{M,eff}}$ which excludes the free volume of the interstices. $V_{\mathrm{M,eff}}$ is very different from V_{M}. It depends on the actual composition of the glass and the production conditions and has often a surprisingly little total of $\approx 0.5\,V_{\mathrm{M}}$. The free or interstitial volume of glasses as well as the interrupts in the silica tetrahedron rings provides an explanation for the remaining deformation of glasses under the tip of an indenter during microhardness tests, for the elastic after-effects of reversible loaded glass bars or springs and for the shrinkage of glass devices during reheating to the transformation range.

Ions have certain mobility in glasses and can move under stress or diffuse at elevated temperature into unoccupied interstices in the glass structure. The ions move only by a few nanometres, sometimes micrometers, which is for most common glass applications not of importance. However, for glass applications in micro devices the ion mobility has to be taken into account.

The density of a glass is not only affected by the chemical composition of the glass and arrangement of the network former (rings!), but also depends on the cooling rate after the products forming. During the cooling of a melt (see Sect. 1.1.4) not only the viscosity increases and the melt transforms from a Newtonian liquid to a brittle–elastic solid, but also its ionic structure changes which is characteristic for any precise temperature of the melt. The structure of the liquid rearranges as the temperature decreases, i.e. the silica tetrahedra become more ordered (but not long-range ordered). The rearrangement of the liquid structure depends on the cooling rate, i.e. how much time is available for this ordering process especially in the Newtonian and the transformation ranges. As a consequence different dense glasses are obtained when cooling a melt faster or slower, see Fig. 1.13. The cooling rate also determines remaining internal (thermal) stresses, which affects the microworkability of glasses in general and the reproducibility of tolerances in micrometer range in particular.

Detailed information about the density of glass melts are given by Pye et al. [414].

1.1.6 Homogeneity of Glasses

The homogeneity of glasses is defined by industrial standards, see also Hoffmann [232]. It is very difficult from the physical point of view to provide a correct definition for a homogeneous glass. What is considered as a homogeneous glass is often difficult to judge and varies with its end-use application. Historically the homogeneity of a glass was defined simply visually. A homogeneous glass is free of any heterogeneities, such as bubbles (blisters, boils or seeds), stones and crystals, striae or cords, which when they are clearly visible are cause for the rejection of the glass. Furthermore colour differences should be avoided if they are visible. On the other hand, however, they might be desired, for instance in antique glass sheets. The size and frequency of