

24.0 cm, weighing 0.902 g, requires 1 min to penetrate 2 cm (used in Germany).

(h) Viscosity $\eta \approx 10^{12} - 10^{13.5}$; T_g (according to German Standard TGL 94-06009). The sample is cooled to room temperature at $1^\circ\text{C} \cdot \text{min}^{-1}$, reheated to determine elongation at $5^\circ\text{C} \cdot \text{min}^{-1}$; T_g is defined as the point at which the elongation becomes discontinuous (Fig. 2.4).

3 Structural Elements of Silicates

When one considers the overwhelming use of silicate glasses in the worldwide production of glasses, an urgent need for the thorough understanding of the structural elements of crystalline silicates is seen. In this respect one deals with one of two comparisons generally mobilized to describe the structure and behavior of glasses: the liquid and the crystalline states of matter. The crystallography of silicates encompasses so vast a body of information that, in the context of glass chemistry, the treatment must be limited to the most necessary foundations. For more information, refer to specialized literature sources (see, for example, Hinz¹³).

The SiO_4 Tetrahedron as the Basic Building Block of Silicates

The basic building block of all silicates is the SiO_4 tetrahedron, i.e., a structural unit with a silicon atom in the center of four surrounding oxygen atoms. All four oxygen atoms simultaneously touch the silicon atom and their external coordinating partners. The bond angles between two oxygen atoms are $109^\circ 28'$; the Si-O bond distance is 0.160 nm (1.60 \AA), and the edge length of the SiO_4 tetrahedron is 0.262 nm (2.62 \AA) (Fig. 3.1).

The origin of this polyhedron and its aggregations, which will be discussed later, are best understood from the consideration of the electronic configuration of silicon and the resulting bonding character.

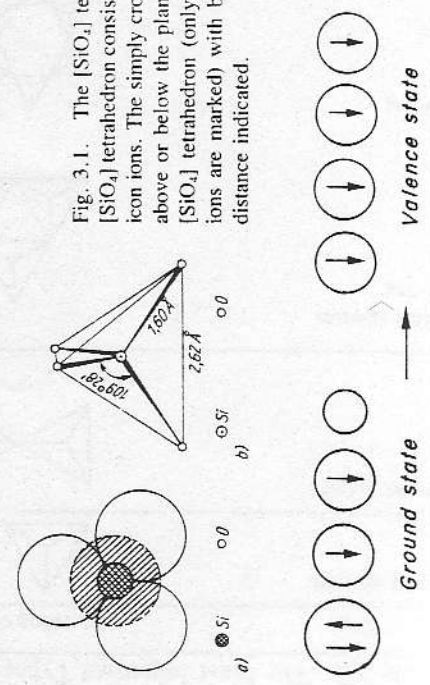


Fig. 3.1. The $[\text{SiO}_4]$ tetrahedron made of $[\text{SiO}_4]$ tetrahedron consisting of oxygen and silicon ions. The simply cross-hatched oxygen lies above or below the plane of the drawing. (b) $[\text{SiO}_4]$ tetrahedron (only centers of charge of ions are marked) with bond angles and ionic distance indicated.

Fig. 3.2. Electronic states of Si and resulting ground and valence states.

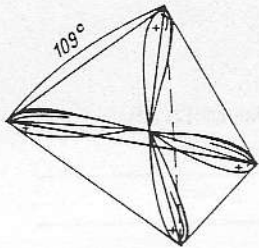


Fig. 3.3. sp^3 hybrid orbitals of Si.

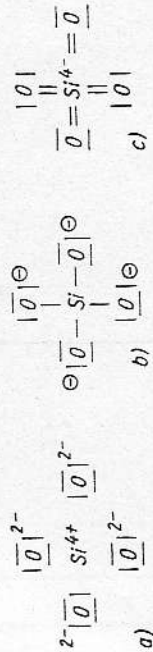


Fig. 3.4. Boundary conditions of bonding in the $[SiO_4]$ complex. (a) Polar; (b) isovalent; (c) double bonding.

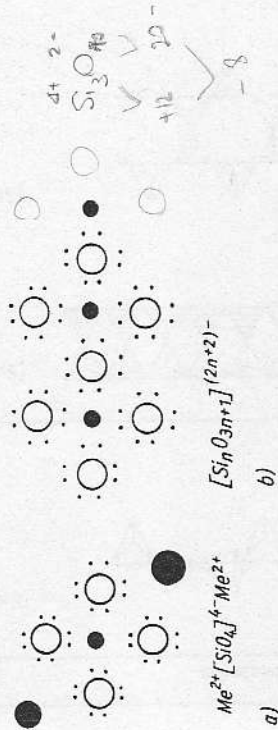


Fig. 3.5. Electron octet formation in silicates. (a) By accepting of electrons from adjacent metal ions; (b) by linking of tetrahedra via bridging oxygen.

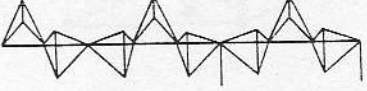
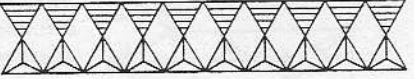
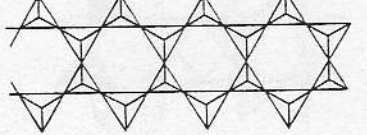
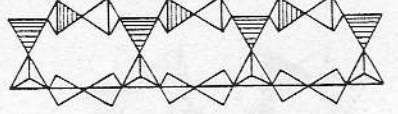
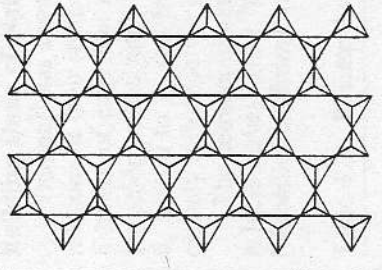
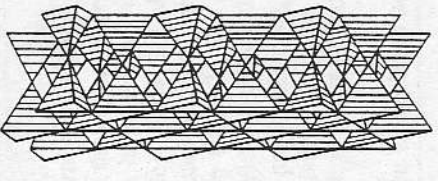
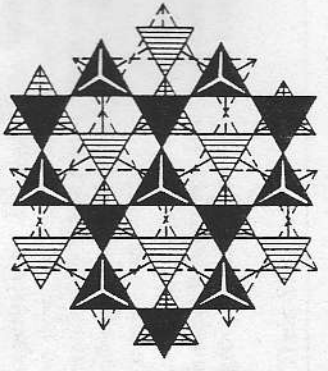
Table 3.1 Dependence of Coordination Numbers on the Ionic Radius Ratios in Crystals

Radius Ratio $r_K:r_A$ as a Boundary Condition for Structure Formed	Coordination Number	Coordination Polyhedron KA_n
≥ 0.155	3	Planar triangle
≥ 0.225	4	Tetrahedron
≥ 0.415	6	Octahedron
≥ 0.732	8	Cube
≥ 1.0	12	Densest packing of spheres

Table 3.2 The Most Important Types of Silicate Structures

Type	Linking of $[SiO_4]$ Tetrahedra	Building Group	Example
Island silicates		$[SiO_4]^{4-}$	Phenacite $Be_2[SiO_4]$ Willemite $Zn_2[SiO_4]$ Forsterite $Mg_2[SiO_4]$
Group silicates		$[Si_2O_7]^{6-}$	Thorveitite $(Sc, Y)_2[Si_2O_7]$
Ring silicates		$[Si_3O_9]^{6-}$ -Ring	β -wollastonite $Ca_3[Si_3O_9]$
6-ring		$[Si_6O_{18}]^{12-}$ -Ring	Beryl $Al_2Be_3[Si_6O_{18}]$
Chain silicates		$[SiO_3]^{2-}$ -chain	Enstatite $Mg_2[Si_2O_6]$ Spodumene $LiAl[Si_2O_6]$

Table 3.2 (continued)

Example	Building Group	Linking of $[\text{SiO}_4]$ Tetrahedra	Type
α -wollastonite $\text{Ca}_3[\text{Si}_3\text{O}_9]$	$[\text{SiO}_3]_2^-$ -chain		Double chain
Sillimanite $\text{Al}[\text{AlSi}_3\text{O}_9]$ $(\text{Al}^{6+})_2[\text{Al}^{3+}\text{Si}_2\text{O}_7]$	$[\text{Si}_2\text{O}_7]_2^-$ -chain		Double binary chain
Tremolite $\text{Ca}_2\text{Mg}_3(\text{OH}, \text{F})$	$[\text{Si}_4\text{O}_{11}]_5^-$ -chain		Double tertiary chain
Xonolith $\text{Ca}_6(\text{OH})_2/\text{Si}_6\text{O}_{17}$	$[\text{Si}_6\text{O}_{17}]_{10}^-$ -chain		Layer silicates Single layer
Talcum $\text{Mg}_3(\text{OH})_2/\text{Si}_4\text{O}_{10}$ Montmorillonite $\text{Al}_2(\text{OH})_2/\text{Si}_4\text{O}_{10}$	$[\text{Si}_2\text{O}_7]_2^-$ -layer		Double layer
$\text{CaAl}_2\text{Si}_2\text{O}_8(\text{hex.})$			Network silicates
High-cristobalite Low-cristobalite High-tridymite Low-tridymite High-quartz Low-quartz	Three-dimensional network $(2\text{SiO}_2 = \text{Si}[\text{SiO}_4])$ $[\text{SiO}_2]_{\infty}$		

The electronic structure of silicon is $1s^2 2s^2 2p^6 3s^2 3p^2$. Relatively little energy is required for the conversion of the ground-state $3s^2 3p^2$ to four unpaired electrons $3s^1 3p^3$ (Fig. 3.2), the spherical s orbital and the three extended p orbitals of which are hybridized to four equivalent orbitals pointing toward the corners of a tetrahedron (Fig. 3.3). In the case of oxygen being the coordination partner, this leads to the stable structural element (SiO_4).

The bond between silicon and oxygen in this tetrahedron is most likely a mixed bond (Fig. 3.4) (Brill et al.¹⁴). Pauling's¹⁵ Si-O value of 0.162 nm (1.62 Å) calculated under the assumption that all three possible bond types occur, agrees quite well with the experimental value of about 0.160 nm (1.60 Å) found for the modifications of crystalline SiO_2 . Similarly, the bond angles agree with those of the model. For purely covalent σ bonding, an angle of 90° would be expected, for pure π bonding one of 180° . Experimental values for Si-O-Si in silicates are between 130° and 140° .

A deeper knowledge of the electronic configuration and the bond type of the SiO_4 tetrahedron is a prerequisite for better understanding its tendency to polymerize and, therefore, form so many complex silicates. The basic principle is the complete saturation of the oxygen atoms with electrons, with a preference for octet shells. On the basis of the bonding conditions shown in Fig. 3.4, this can be realized by either (a) metals neutralizing the complex by joining the SiO_4 complex, or (b) a connection of the tetrahedra themselves via "oxygen-bridges" forming octets of electrons (Fig. 3.5). If giant molecules are formed in this manner, it only remains to saturate terminal tetrahedra directly by metal atoms.

Building Units of Natural Crystalline Silicates

Pauling¹⁵ has shown that the packing density of two ions depends on the relations of their radii. A large number of experimental data led to the establishment of empirical rules. Table 3.1 shows how, on exceeding certain cation:anion radius ratios, coordination numbers change from 3 to 4, from 4 to 6, from 6 to 8, and from 8 to 12. The resulting coordination polyhedra decisively influence the crystal structure of a compound.

The tetracoordinate polyhedra SiO_4 can be connected in various ways. A lucid survey (Hinz¹³) distinguishes the following basic types: island silicates (nesosilicates, from Greek *nesos* = island), group silicates (sorosilicates, from

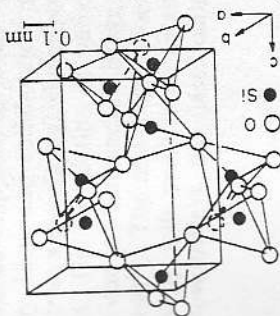
Table 3.3 Silicate Anion Complexes and Their Si : O ratios

Type	Formula Anion of Complex	Si (or Si + Al) : O Ratio	Number of Bridging Oxygens
Island silicates	$[\text{SiO}_4]^{4-}$	1 : 4	0
Group silicates	$[\text{Si}_2\text{O}_7]^{6-}$	1 : 3.5	1
Ring silicates	$[\text{SiO}_3]^{2-}$	1 : 3	2
Chain silicates	$[\text{SiO}_3]^{2-*}$	1 : 3	2
Layer silicates	$[\text{Si}_2\text{O}_5]^{2-\infty}$	1 : 2.5	3
Network silicates	$[\text{SiO}_2]_{\infty}$	1 : 2	4

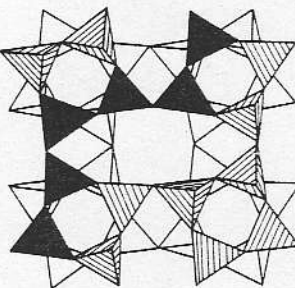
*Subscripts ∞ mean 1-, 2-, or 3-dimensional linkage.

Orthoclase- KAlSi_3O_8 plagioclase (mixed crystals between albite $\text{NaAlSi}_3\text{O}_8$ and anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$)

Structure of β -cristobalite (Low cristobalite)



Structure of α -cristobalite (High cristobalite)



Linking of $[\text{SiO}_4]$ Tetrahedra

Type

Building Group

Example

Table 3.2 (continued)

Greek *soros* = group), ring silicates (cyclosilicates, from Greek *kyklos* = circle), chain silicates (inosilicates, from Greek *inos* = fiber), layer silicates (phyllosilicates, from Greek *phylon* = block), and network silicates (tectosilicates, from Greek *tektoneia* = lattice).

The basic structural types are encountered in numerous natural and synthetic silicates.

Table 3.2 gives a typical example for each kind. Table 3.3 lists the resulting Si:O relations and the formulas for the anion complexes resulting from various extensive connections. A systematic classification by anion complex required the development of X-ray diffraction as a tool for structural investigation by Laue and collaborators (since 1912). Until then silicates were classified from a morphological viewpoint and oxide formulas such as $\text{CaO} \cdot \text{SiO}_2$ were used. The elucidation of numerous silicated structures by X-ray diffraction is due to Machatschki, Bragg, and their collaborators (Warren et al.,¹⁷ Machatschki¹⁸). The now conventional formulation, e.g., $\text{Ca}_3(\text{Si}_3\text{O}_9)$ instead of $\text{CaO} \cdot \text{SiO}_2$, tells much more about the degree of polymerization of anion groups. Nevertheless, the classification of silicates remains an open field.

4 Classical Theories of Glass Structure 33

Glass Structure According to Tammann (since 1903) (Refs. 6–8)

Tammann, the first investigator concerned with the constitution of glasses, regarded them as strongly undercooled liquids. To a certain degree this is in agreement with later interpretations using X-ray diffraction data. At that time the structures of liquid crystals and of liquids of Bernal, Stewart, or Frenkel type (which will be discussed later) were not yet known. Tammann's model of the freezing-in of a structure quite similar to that of the liquid was quite general, but did represent a good start.

Tammann also was the first to investigate low-melting-point model glasses, organic glasses obtained by rapid cooling of molten piperidine, salicin, phenolphthalein, sugars, etc. These investigations resulted in fundamental information about nucleation and crystallization of glasses (see Chapter 2, Fusion and Crystallization).

Glass Formation According to Goldschmidt (Ref. 20) (1926)

Goldschmidt, who is considered the founder of modern crystal chemistry, was in a position to derive empirical rules for glass formation from his studies. Just as in the case of crystal structure, relations of ionic size were to play a decisive role. He postulated a ratio of from 0.2 to 0.4 of radius-of-cation (r_c) to radius-of-anion (r_a) as a condition of glass formation. This condition is fulfilled in the case of SiO_2 , B_2O_3 , P_2O_5 , etc. (Table 4.1).

The Zachariasen-Warren Network Theory (1932)

The network hypothesis proposed by Zachariasen²¹ and reinforced by Warren's²² X-ray diffraction represented a leap forward in the knowledge about the structure of glasses. For instance, in the case of SiO_2 glass the same tetrahedra which are uniformly connected in crystalline silicates (Fig. 4.1(a), Bragg) are connected irregularly (Fig. 4.1(b)). The formation of a 3-dimensional disordered infinite network from building units of low coordination number (e.g., 4 in SiO_4 tetrahedra, or 3 in BO_3 triangles) explained convincingly the enormous increase in viscosity on cooling.

According to the Zachariasen-Warren network theory, the following rules are valid for the formation of low-order 3-dimensional networks, i.e., the glass formation of simple compounds such as SiO_2 , B_2O_3 , P_2O_5 , GeO_2 , As_2S_3 , BeF_2 :