Optical and Photonic Glasses

Lecture 5:

Structures of Glass I

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Wrap up from last lesson

Sol-gel glasses (contd)

The colloidal route designated by *sol-gel* is a method for preparing glasses, either in bulk or thin film form, which assumes special importance in the case of optical and photonic glasses.

The traditional sol-gel process, whose origin dates back to the 19th century, may be exemplified in the case of the preparation of SiO_2 glass. This starts with the hydrolysis and polycondensation of an alkoxide such as tetraethoxy-silane (TEOS) in an acidic medium:

$$Si(C_2H_5O)_4 + 2\,H_2O \;=\; SiO_2 + 4\,C_2H_5OH \;\overset{\Delta}{\rightarrow}\; \text{dry gel} \;\overset{\Delta}{\rightarrow}\; \text{dense } SiO_2 \text{ glass}$$

A coloidal solution (the “sol”) is first obtained, which polymerizes further (“ageing”) and turns into a “gel” (through solvent evaporation); this is further dried and finally densified (at a temperature near T_g) into a solid, dense glass.

Glass structure

In a glassy material, one can in principle distinguish three ranges of order:

- short range order (SRO)
- intermediate range order (IRO)
- long range order (LRO)

In a *single phase glass*, LRO, which is related to density and composition fluctuations, is basically absent. IRO, on the other hand, which refers to preferred (non-random) distributions of structural features such as angles between coordination polyhedra (bridging or dihedral), or the ring statistics, may in fact be present, but it will not concern us at this stage. We will, therefore, be mostly concerned with the **SRO**, which **defines** the **basic structural unit** or building block of the glass, in terms of: (1) CN; (2) geometry of nearest neighbor coordination polyhedra; (3) bond angles; (4) bond lengths.

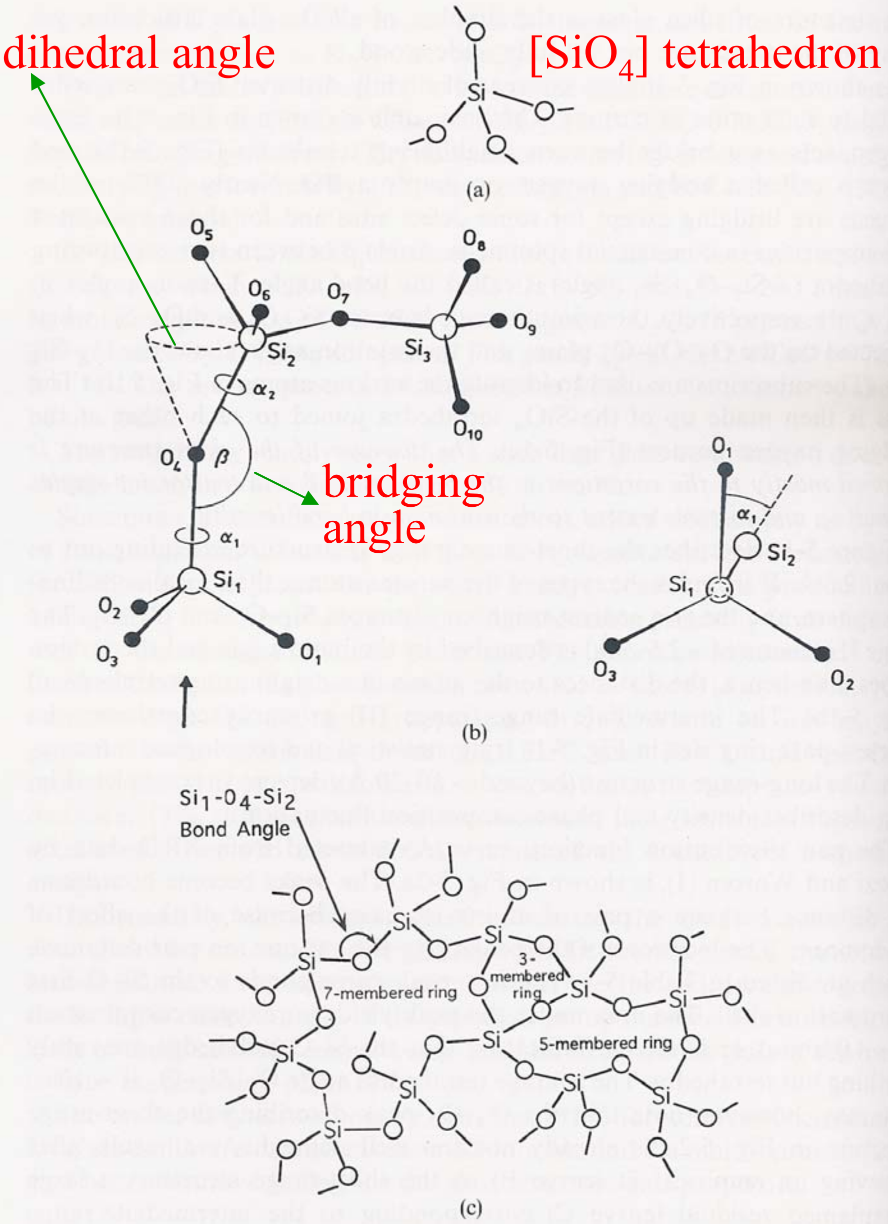
Short range order

Typical examples of SRO features in glass are the [SiO_4] tetrahedron in silica glass, where CN_{Si} = 4, all the O-Si-O angles have the tetrahedral value of $109^o28'$ and all Si-O bonds have the same length ~ 0.162 nm.

The fact that it has been found that the Si-O-Si ("bridging") angles present a relatively broad (but non-random) distribution, from ~ 120^o-180^o, is a IRO feature of v-SiO_2, rather than SRO.

Strictly speaking, in a modified silicate glass like 2 SiO_2-Na_2O (called a "disilicate"), the fundamental structural unit is no longer a tetrahedron, but rather a trigonal pyramid, as one will see later on.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)


dihedral angle

[SiO$_4$] tetrahedron

bridging angle

(a) Basic building block for silica glass. SiO$_4$ tetrahedron with all four oxygens bridging between neighboring tetrahedra. (b) Definition of the bond angle β and the torsion angles α_1 and α_2. (After A. C. Wright, G. A. N. Connell, and J. W. Allen, *J. Non-cryst. Sol.* **42**, 69 (1980). Reproduced with permission of Elsevier Science Publishers.) (c) Schematics of the silica glass network, defining the "bond angle" and the ring structures.

Structure of NCS - XRD analysis

Although the **XRD** patterns of a glass contain only a few, very broad peaks, which cannot be correlated with distances between (inexistent) interatomic planes (as in the case of a crystalline material), it is possible to extract structural information from such patterns by means of Fourier analysis of the data.

After correcting the raw intensity data, $I(\theta)$ (in *reciprocal* space), these are Fourier transformed into real space, yielding the so-called **Radial Distribution Function** (RDF):

$$RDF(r) = 4 \pi r^2 \rho(r)$$

where $\rho(r)$ is the glass number density, or the number of atoms per unit volume at a distance r from an arbitrary origin atom.

Whereas the RDF is a 1-D representation of the glass structure, a more refined analysis may lead to the *pair correlation functions*, which provide a more detailed and specific description of the glass structure and may be directly compared to theoretical simulations, e.g. by means of molecular dynamics (MD).

The total correlation function, T(r), shown in figure (a):

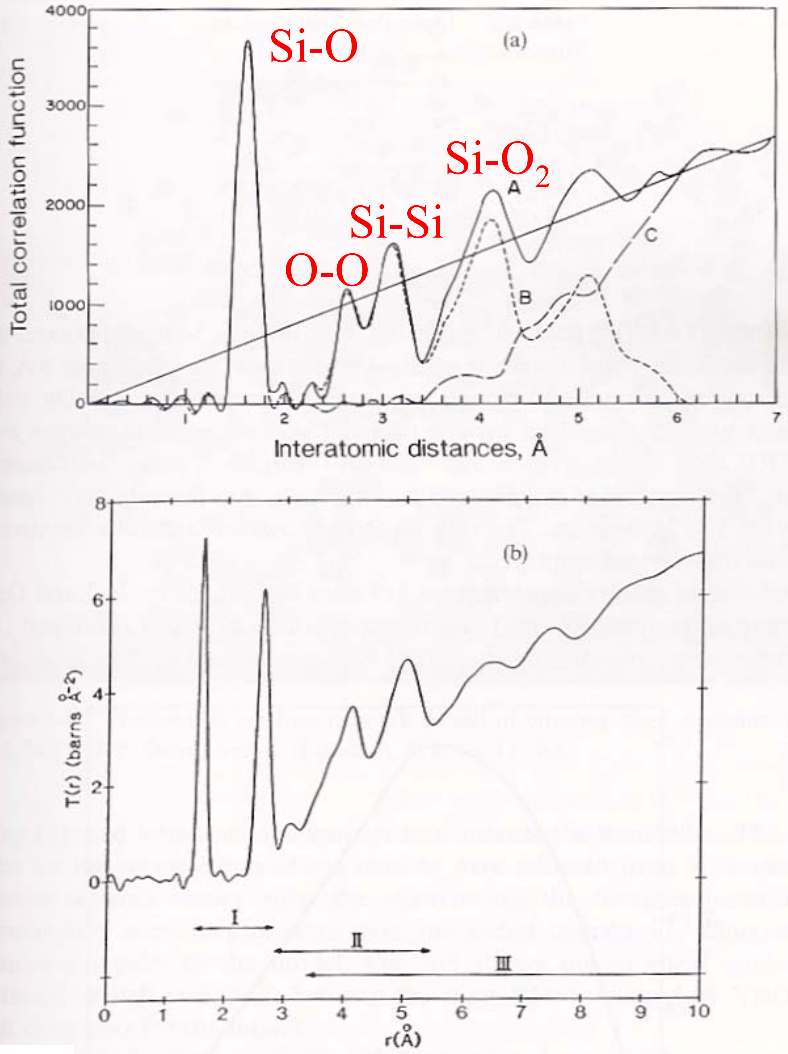
$$T(r) = 4 \pi r \rho(r)$$

is slightly different from RDF, as it oscillates about a straight line, whereas RDF(r) oscillates about a parabola. The value of **RDF(r)** represents the **probability** of **finding an atom** of the glass in a **spherical shell** of radius r and unit thickness, at a distance r of the origin atom.

The CN_{Si} is proportional to the area under the 1st peak @ ~ 0.162 nm, found to be ~ 4.0, corresponding to a [SiO_4] tetrahedron.

Neutron diffraction (ND) is another independent method to obtain RDF(r), or T(r), shown in figure (b).

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)



[redacted] (a) The total correlation function for fused silica, measured by Mozzi and Warren (1) using x-ray. A is the measured curve; B is the sum of the calculated curve for the six contributions: Si_1–O_1, O_1–O_2, Si_1–Si_2, Si_1–O_6, O_1–O_6, and Si_1–Si_3. Curve C is the difference between A and B. (Reproduced with permission of Munksgaard International Publishers Ltd., Copenhagen.) (b) The total correlation function of fused silica measured using neutron diffraction. The roman numerals define the various ranges of structures. Note a better definition of the O_1–O_2, and not so good a definition of the Si_1–Si_2 peak. (After A. C. Wright, R. A. Hulme, D. I. Grimley, R. N. Sinclair, S. W. Martin, D. L. Price, and F. L. Galeener, *J. Non-cryst. Sol.* **129**, 213 (1991). Reproduced with permission of Elsevier Science Publishers.

The X-ray RDF data of Mozzi and Warren were interpreted in terms of the CRN model of Zachariasen. A fitting of the 3rd (Si-Si) and 4th ($Si-O_2$) peaks in RDF(r) led to the following most probable distribution of the Si-O-Si bridging angles, a feature of the IRO of fused silica.

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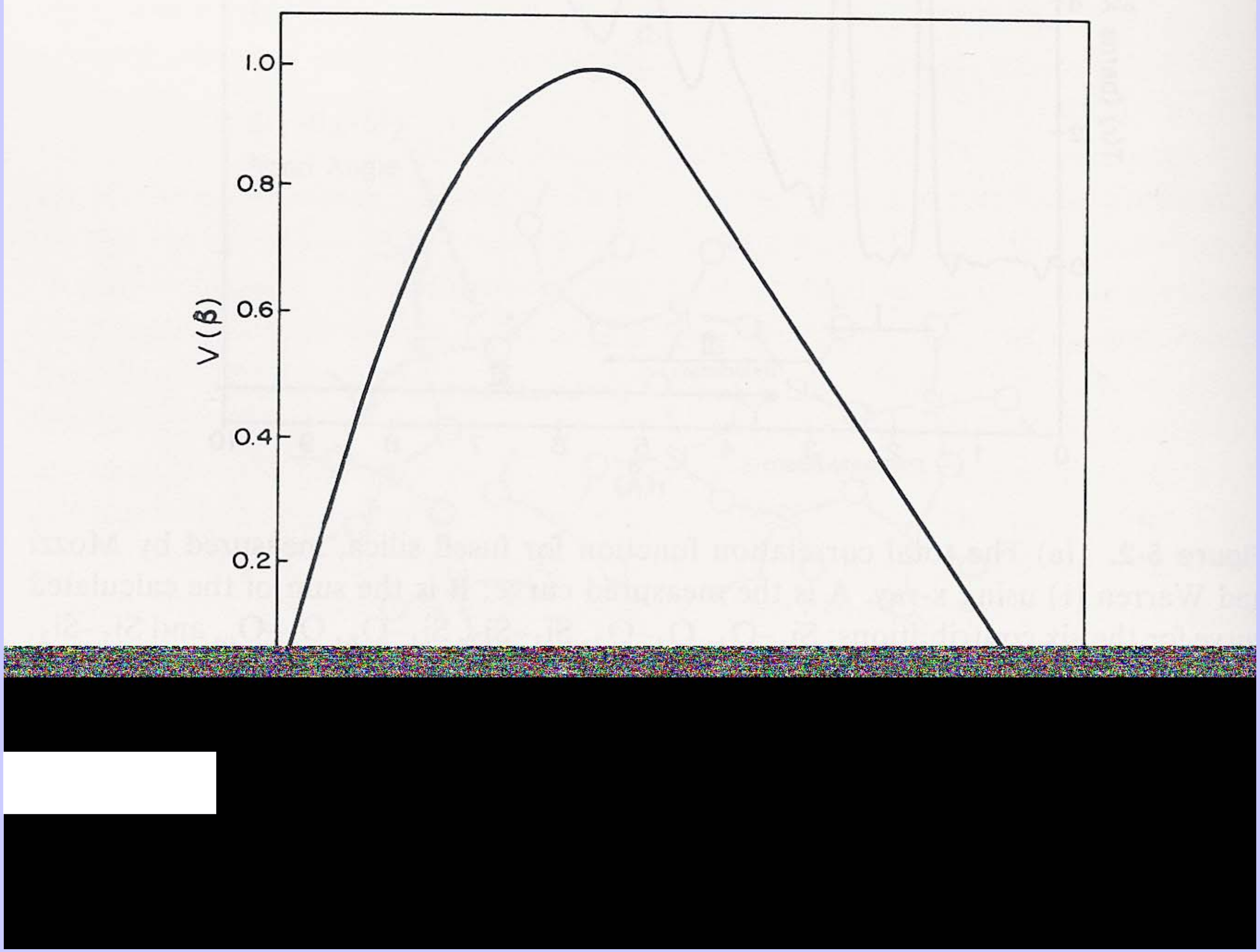
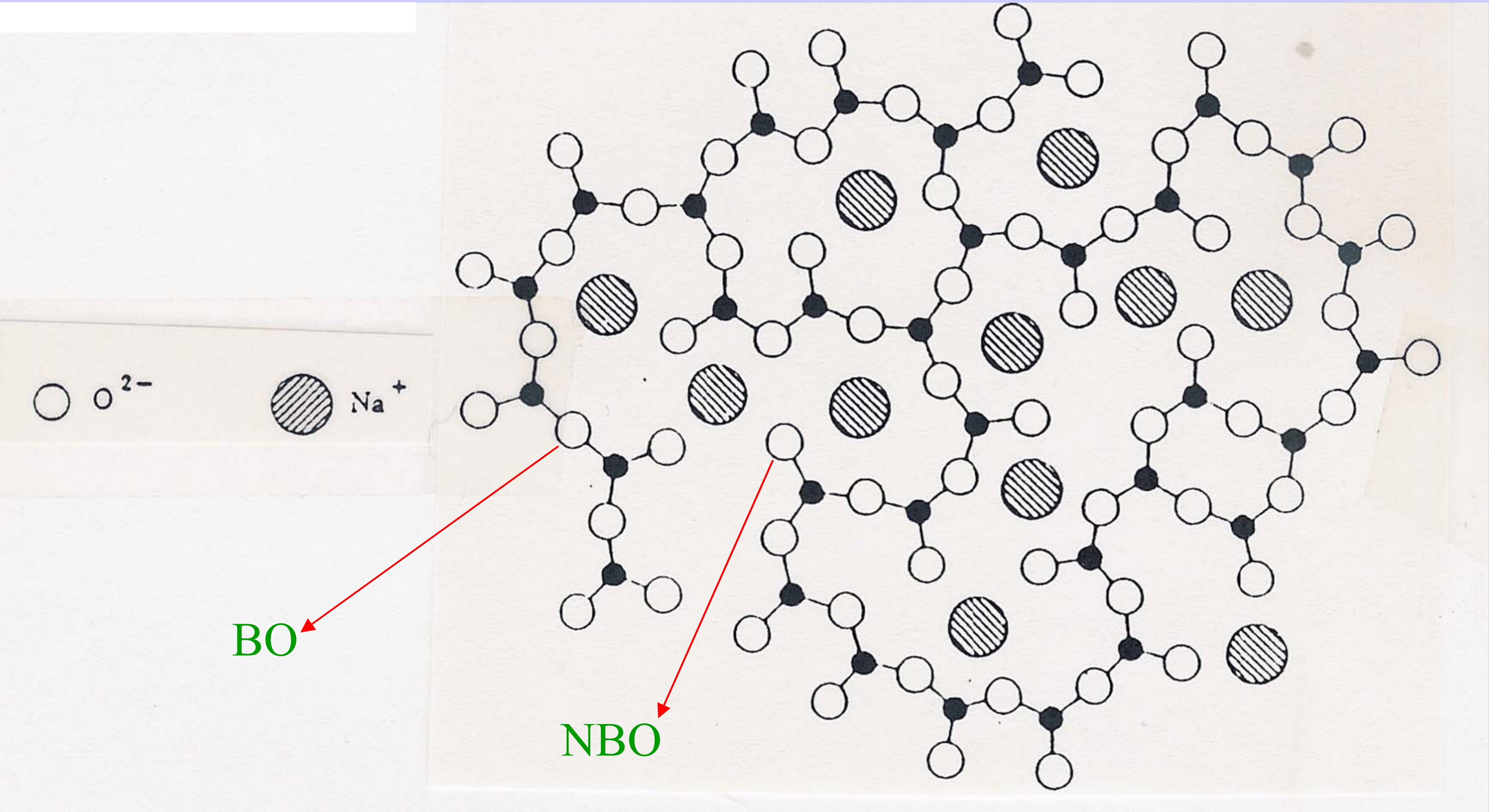


Structure of modified silicate glasses

Below is a SiO_2-Na_2O **modified glass**, where the Na^+ modifying ions caused a structural breakdown of the 3-D silica network:

$$\equiv\text{Si-O-Si}\equiv + Na_2O \rightarrow \equiv\text{Si-O}^{-Na+}\ {}_{Na+}O^{-}\text{-Si}\equiv$$

leading to lower viscosity and lower T_g values for the glass.



Designations for **modified silicate glasses**

Example of alkaline-earth silicates ($MO.SiO_2$, in mol%):

	example	designation	net. dimens.	# BO/tetr.	symbol
0 % MO →	SiO_2	(silica)	3-D	(4 BO/tetr.)	Q_4
33 % MO →	$CaO.2\ SiO_2$	(disilicate)	2-D	(3 BO/tetr.)	Q_3
50 % MO →	$CaO.SiO_2$	(metasilicate)	1-D	(2 BO/tetr.)	Q_2
60 % MO →	$3\ CaO.2\ SiO_2$	(pyrosilicate)	dimers	(1 BO/tetr.)	Q_1
66 % MO →	$2\ CaO.SiO_2$	(orthosilicate)	monomers	(0 BO/tetr.)	Q_o