Optical and Photonic Glasses

Lecture 1:

Intro to Glass and the Glass Transition

Professor Rui Almeida

International Materials Institute
For New Functionality in Glass
Lehigh University

Program

- **Glass and amorphous materials**
  - What is glass
  - Composition and preparation
  - Structure
  - Properties
- **Optical glass: fabrication and optical properties**
  - Traditional optical glasses
  - New optical glasses
  - Abnormal dispersion glasses
  - Transparent glass ceramics
- **Photonic glasses**
  - Gradient index glass and fiberoptic glasses
  - Photosensitive glasses
  - Acousto-optical and magneto-optical glasses
  - Laser glasses
  - Non-linear optical glasses

Detailed course syllabus

What is glass: definition, glass formation, Tg, regions of glass formation, theories of glass formation.

Glass composition and preparation: glass formers, modifiers and intermediates; preparation of oxide glasses (melting, sol-gel, CVD, …); flat glass, hollow glass, fiber glass.

Glass structure: structure of network oxide glasses; X-ray diffraction analysis; structure of modified oxide glasses (silicates, borates, aluminosilicates, phosphates, …), fraction of NBO atom species; glass-in-glass phase separation, Vycor glass; glass-ceramics.

Basic glass properties: density; mechanical behavior; viscosity; thermal expansion.

Traditional optical glasses: composition and fabrication; optical properties (refractive index, reflection, scattering, absorption - electronic, vibrational, Raman scattering).

New optical glasses: preparation of non-oxide glasses (fluorides and chalcogenides); specific properties (mechanical behavior, viscosity, Tg, IR transmission).

Abnormal dispersion glasses: abnormal dispersion in phosphate based glasses; athermal glasses.

Transparent glass ceramics: Pr-doped oxyfluoride glass ceramics; other transparent GC's doped with Er, Yb, Tm and Eu.

Gradient index glass and fiberoptic glasses: GRIN glasses by ion exchange and sol-gel; guided wave optical glasses; glass fiberoptics; integrated optical glass waveguides. **Photosensitive glasses:** photochromic glasses; permanent refractive index changes in germania containing glasses; Bragg gratings; photoinduced effects in chalcogenide glasses (photocontraction, photoexpansion, …).

Acousto-optical and magneto-optical glasses: acousto-optical and delay line glasses; Faraday rotation in glass; paramagnetic glasses; optical isolators.

Laser glasses: rare-earth doped glasses (Nd, Er, Yb, Tm, Pr, …); photoluminescence of rare-earth ions in glass; laser effect in glass; optical amplification in glass; glass fiber lasers and fiber amplifiers; glass waveguide lasers and amplifiers.

Non-linear optical glasses: fundamentals of NLO; non-resonant optical non-linearity; non-linear refractive index; resonant optical non-linearity; semiconductor-doped glasses (strong confinement case, photodarkening, weak confinement case); metal-doped glasses; NLO properties of metal-doped glasses (electric field enhancement and quantum confinement effects).

Relevant books

T.S. Izumitani, **Optical Glass**, American Institute of Physics Translation Series (New York, 1986).

Masayuki Yamane and Yoshiyuki Asahara, **Glasses for Photonics**, Cambridge University Press (Cambridge, U.K., 2000).

K. Booth and S. Hill, **The essence of optoelectronics**, Prentice Hall (London, 1998).

R. Tilley, **Colour and the optical properties of materials**, John Wiley (New York, 2000).

J.H. Simmons and K.S. Potter, **Optical Materials**, Academic Press (New York, 2000).

M. Fox, **Optical properties of solids**, Oxford University Press (Oxford, UK, 2001).

A.K. Varshneya, **Fundamentals of Inorganic Glasses**, Academic Press (New York, 1994).

James E. Shelby, **Introduction to Glass Science and Technology**, The Royal Society of Chemistry (Cambridge, U.K., 1997).

Glass and amorphous materials

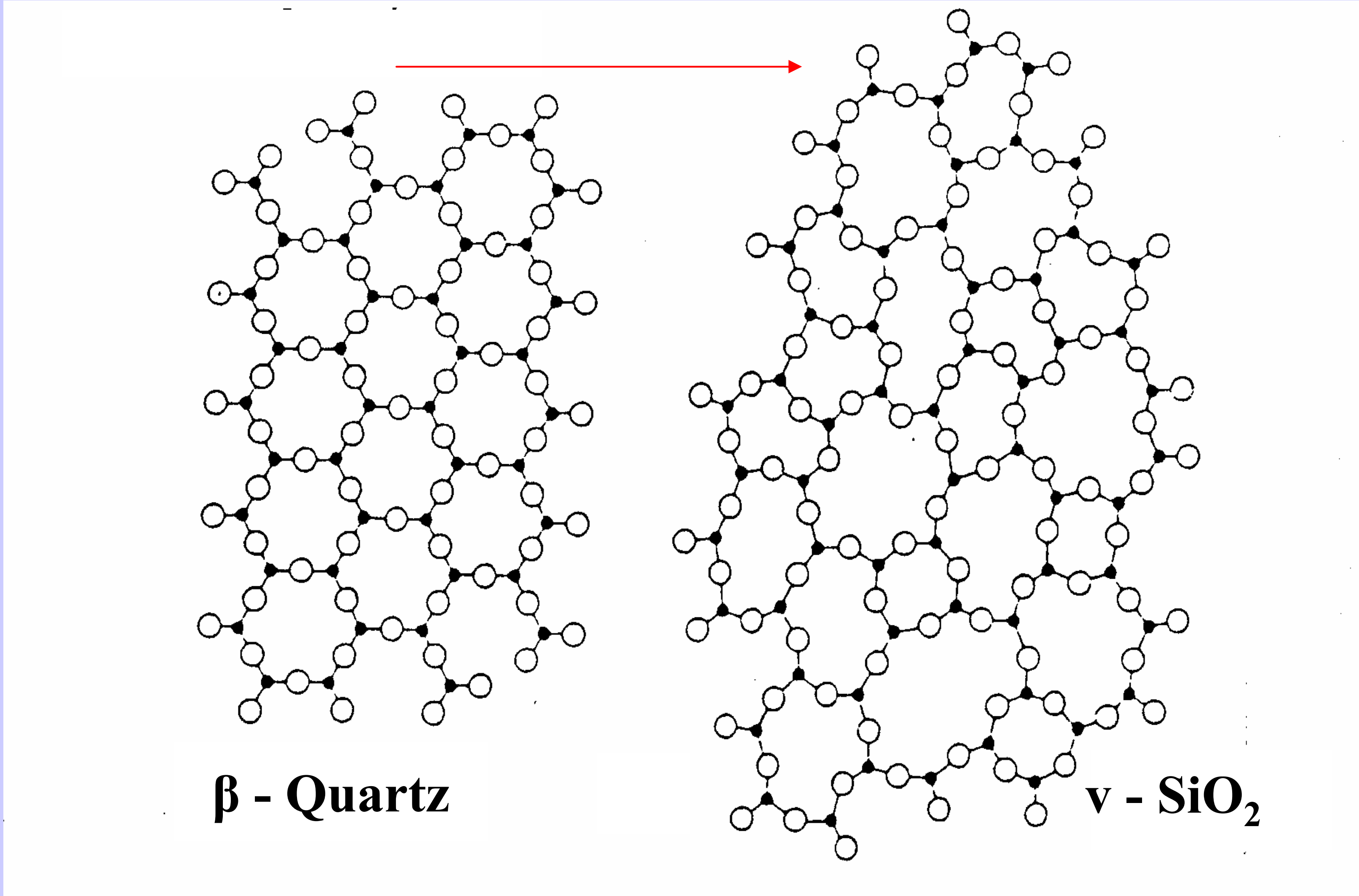
What is glass?

A **glass**, whether in *bulk, fiber or film* form, is a **non-crystalline solid (NCS)**. In principle, any substance can be vitrified by quenching it from the liquid state, while preventing crystallization, into a solid glass. A glass is, therefore, a non-crystalline (or amorphous) solid.

Most commercially available glasses, are prepared by melting and quenching. But deposition from a vapor or a liquid solution are alternative methods to obtain glasses, usually in thin film form, some of which may otherwise be rather difficult to prepare from the melt.

Glass formation, although in principle a property of any material, is in practice limited to a relatively small number of substances. And most commercial glasses, available in large bulk shapes, are silicates of one type or another, i.e., materials based on silica, the oxide SiO_2.

The structural transformation of silica from crystal to glass



Glass forming systems

Below are some of the most representative glass-forming substances known to date.

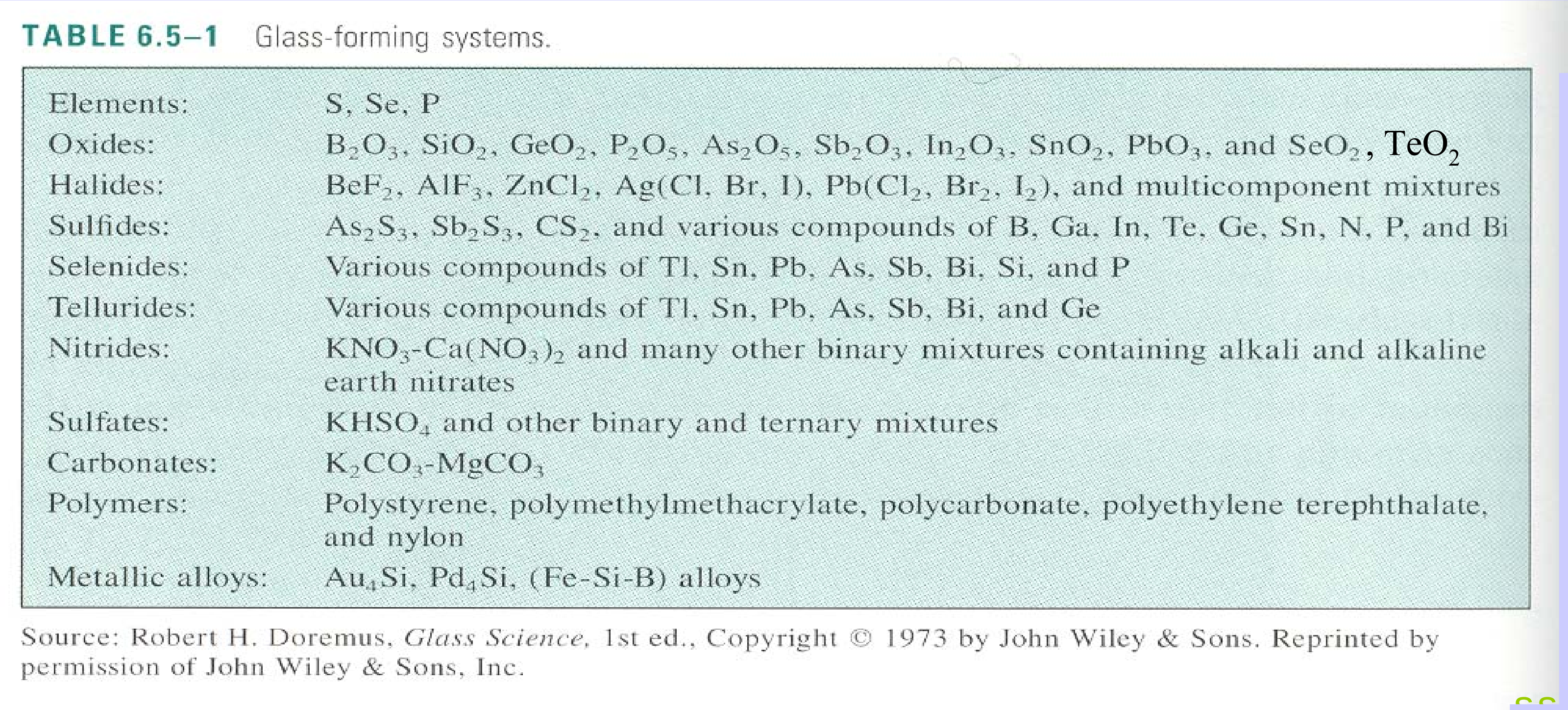


TABLE 6.5–1 Glass-forming systems.

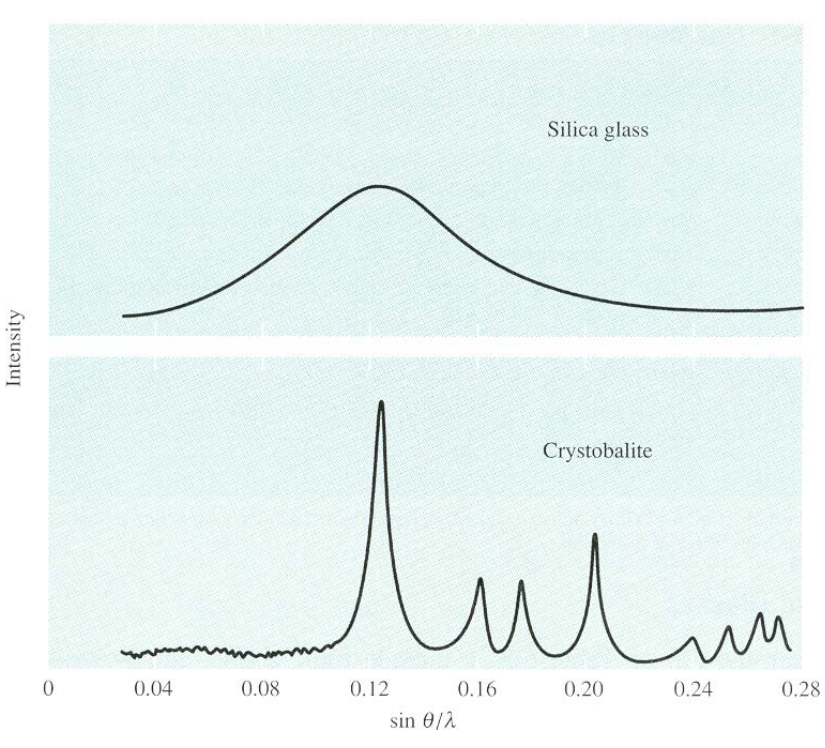
Elements:	S, Se, P
Oxides:	B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, Sb_2O_3, In_2O_3, SnO_2, PbO_3, and SeO_2, TeO_2
Halides:	BeF_2, AlF_3, $ZnCl_2$, Ag(Cl, Br, I), Pb(Cl_2, Br_2, I_2), and multicomponent mixtures
Sulfides:	As_2S_3, Sb_2S_3, CS_2, and various compounds of B, Ga, In, Te, Ge, Sn, N, P, and Bi
Selenides:	Various compounds of Tl, Sn, Pb, As, Sb, Bi, Si, and P
Tellurides:	Various compounds of Tl, Sn, Pb, As, Sb, Bi, and Ge
Nitrides:	KNO_3-$Ca(NO_3)_2$ and many other binary mixtures containing alkali and alkaline earth nitrates
Sulfates:	$KHSO_4$ and other binary and ternary mixtures
Carbonates:	K_2CO_3-$MgCO_3$
Polymers:	Polystyrene, polymethylmethacrylate, polycarbonate, polyethylene terephthalate, and nylon
Metallic alloys:	Au_4Si, Pd_4Si, (Fe-Si-B) alloys

Source: Robert H. Doremus, *Glass Science*, 1st ed., Copyright © 1973 by John Wiley & Sons. Reprinted by permission of John Wiley & Sons, Inc.

(Adapted from: *The science and design of engineering materials*. J.P. Schaffer et al., McGraw-Hill, 1999)

One of the best experimental tools to distinguish a glass (or NCS) from a crystalline material is X-ray diffraction (XRD). In the case of silica, one has the following XRD patterns:

(Adapted from: *The science and design of engineering materials*, J.P. Schaffer et al., McGraw-Hill, 1999)



The patterns of silica glass are a very broadened and smeared version of those of the high temperature crystalline form, crystoballite. This is also a strong indication that the atomic scale *short range order* is the *same* in the glassy and crystalline forms of solid silica.

It is important to realize that some materials which have a very strong glassy appearance under the naked eye, or even under a laser beam (such as the He-Ne red light @ 633 nm), may actually contain a fine dispersion of very minute crystals with dimensions well below 100 nm, i.e., **nanocrystals**.

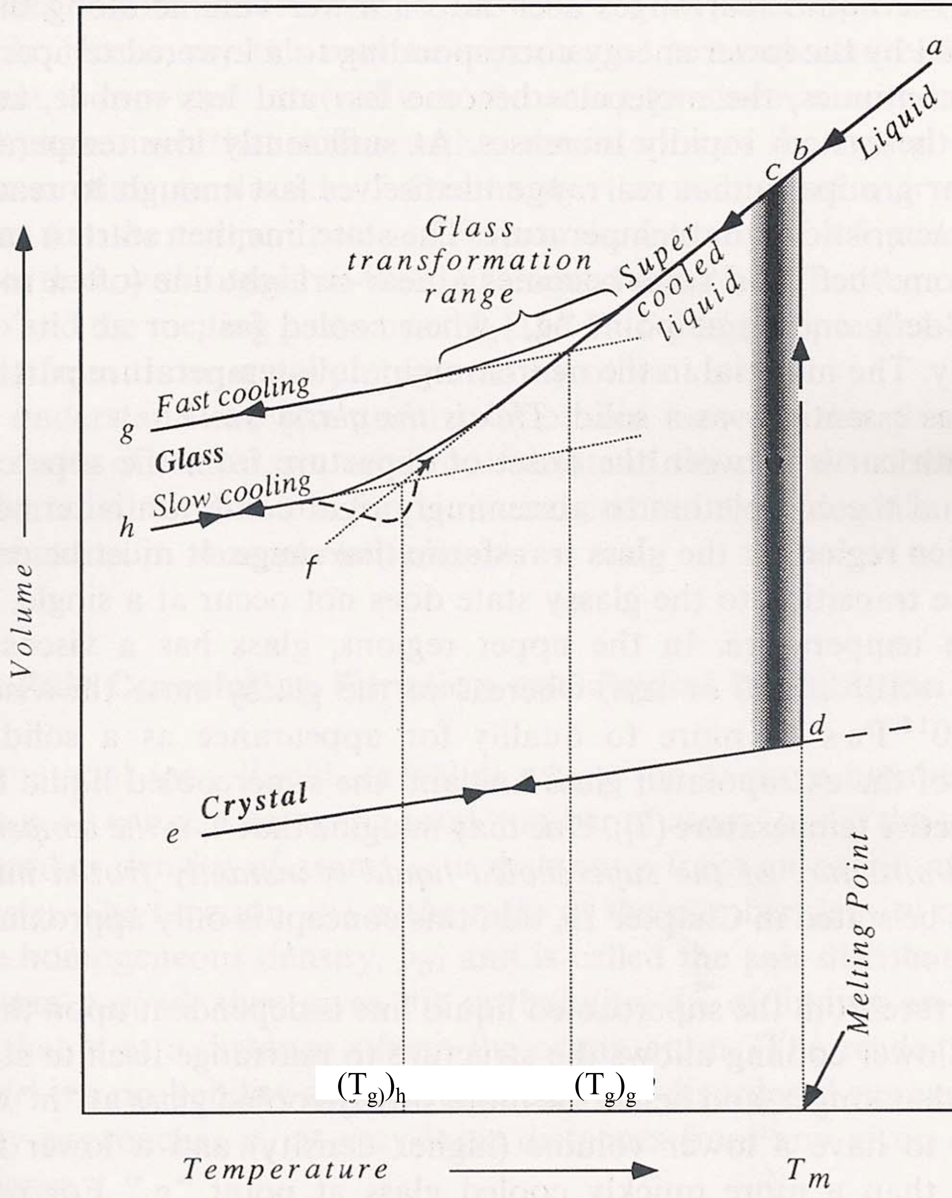
Such **nanocomposite** materials may be very difficult to differentiate from a 100% glassy material, even using XRD. However, their nanocrystalline nature may be identified by means of a microscopic method such as Transmission Electron Microscopy (TEM), after suitable (and often time-consuming) sample preparation.

Glass transition temperature

Most commercially available glasses are NCS obtained by rapid solidification of a viscous liquid below a given "freezing" temperature, designated by Glass Transition Temperature, T_g. We shall see that T_g is often ~ 2/3 of the melting (or the liquidus) temperature, T_m.

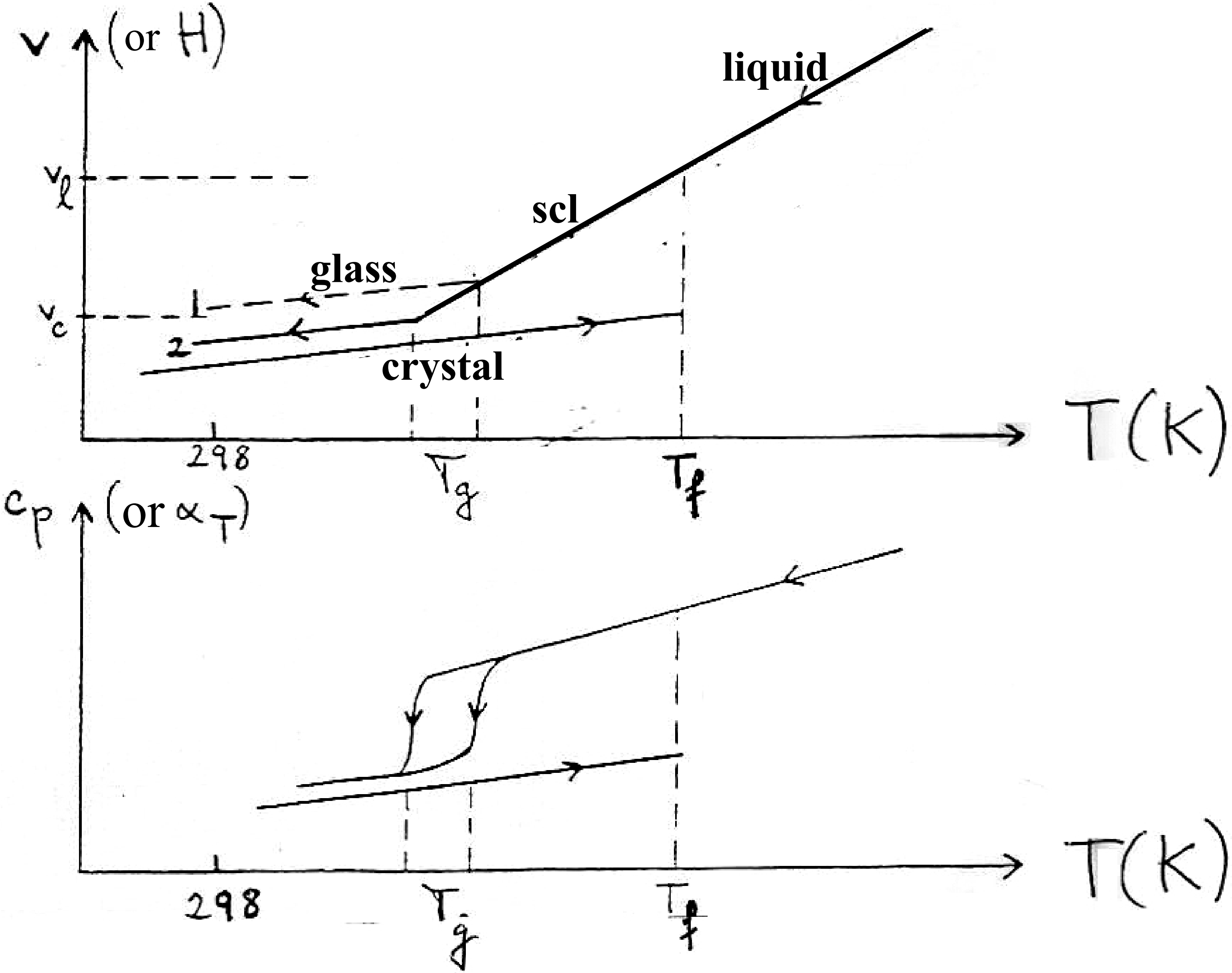
The liquid of rapidly increasing viscosity which is obtained between T_m and T_g is called a *supercooled liquid*. T_g marks, therefore, the transformation from the supercooled liquid into the solid glass.

The preparation of glasses by melting and quenching may be understood by plotting the volume (or the enthalpy), or their corresponding derivatives, the thermal expansion coefficient, α_T (or the specific heat, c_p), as functions of temperature.



The volume–temperature diagram for a glass-forming liquid.

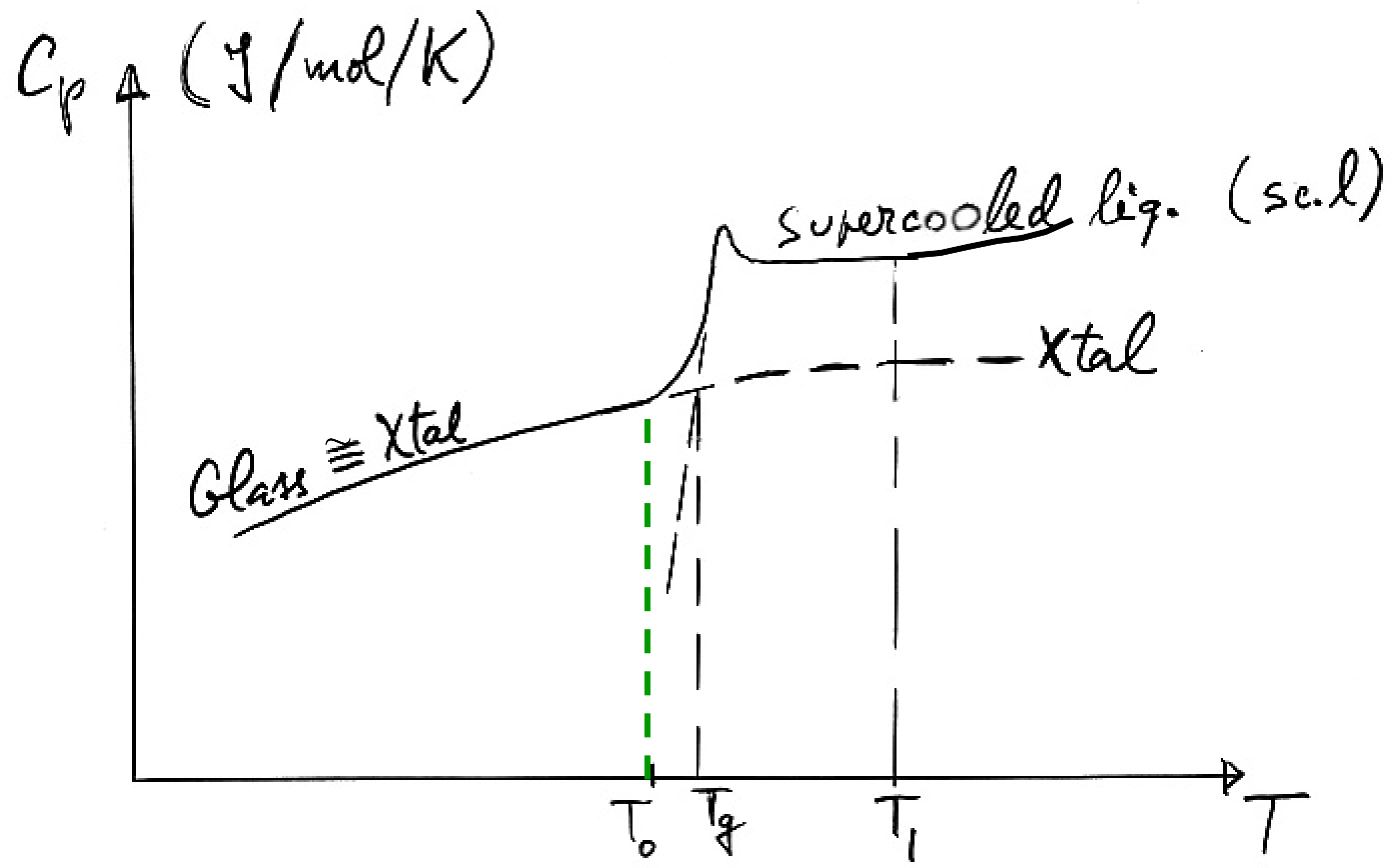
(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)


V (or H)
liquid
V_ℓ
scl
glass
1
V_c
2
crystal
T(K)
298
T_g
T_f
c_p (or α_T)
T(K)
298
T_g
T_f

Important points to bear in mind about the nature of the temperature range designated as T_g:

Unlike T_m, which represents a first order thermodynamic transition, accompanied by a discontinuity in the specific volume, v, **T_g** is **not** a **well defined temperature**, but rather a temperature range. The faster the quenching of the liquid, the higher the T_g value of the glass obtained. T_g, therefore, **depends on the** actual **rate of cooling** of the supercooled liquid. T_g also represents the highest useful temperature for the utilization of a glass.

The appearance of the temperature range around T_g, where c_p (the first derivative of the enthalpy, $(\partial H/\partial T)_p$), has a pronounced drop (or an apparent discontinuity) can be considered as a kinetic necessity, in order to avoid a violation of the third principle of thermodynamics. This is, in essence, the reasoning associated with the **Kauzmann paradox.**



$$S_{scl}^{T_1} - S_{xtal}^{T_1} = \int_{T_o}^{T_1} (C_p^{scl} - C_p^{xtal})\, dT/T$$

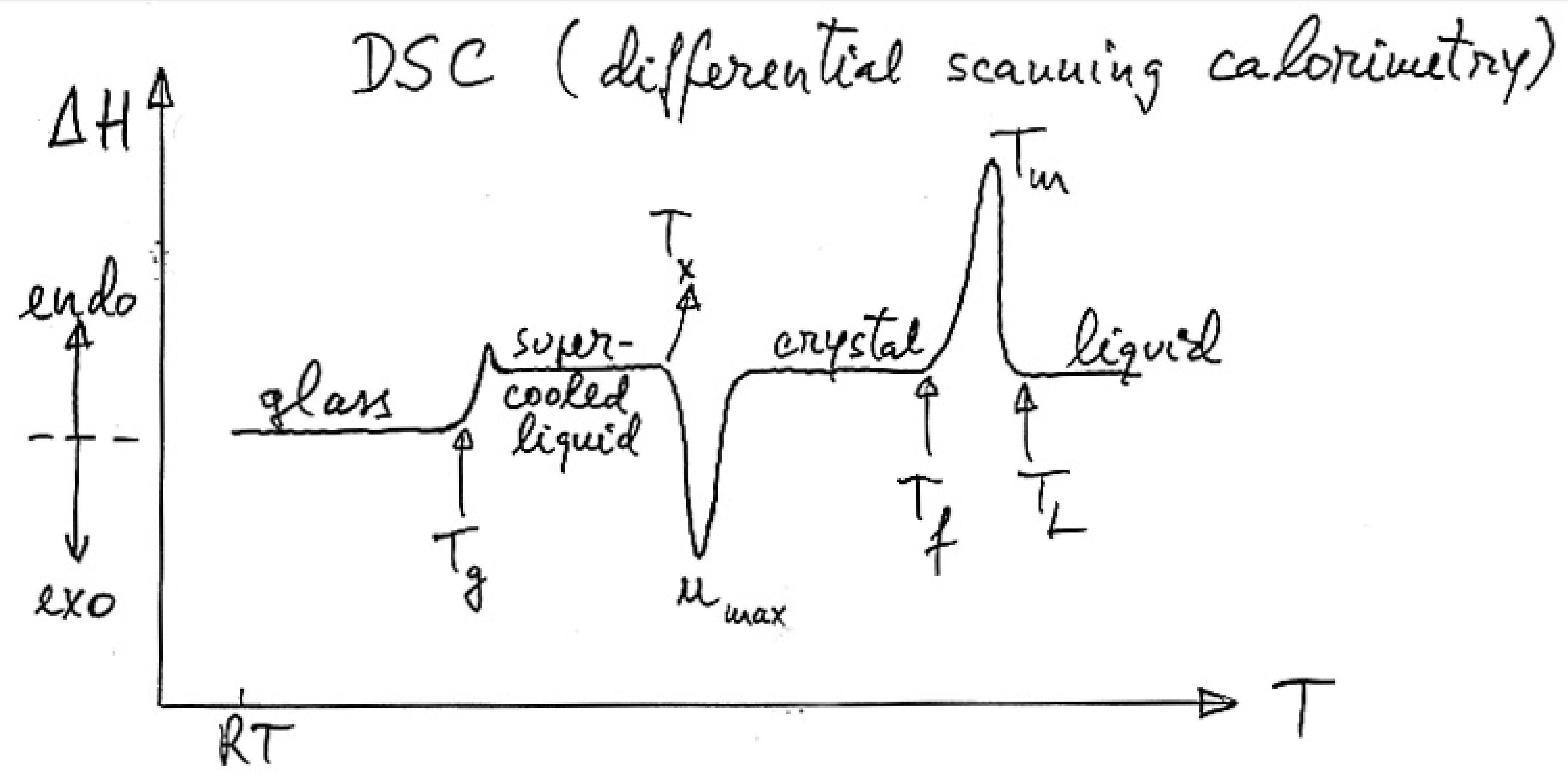
Kauzmann paradox: if there were no sudden drop in c_p at T_g, the **entropy** of the **scl** would eventually fall below that of the crystal, being negative at 0 Kelvin, when the third law requires $S_{xtal} = 0$. (The glass has a positive residual entropy at 0 Kelvin).

T_o → lowest limit of T_g, for *infinitely* slow cooling.

(VFT equation: $\eta = \eta_o \exp Q/(T-T_o)$ $T \rightarrow T_o \Rightarrow \eta \rightarrow \infty$ and $V_f \rightarrow 0$)

The value of T_g for a given glass can be obtained, for example, from a measurement of its thermal expansion coefficient, as we shall see later.

T_g can also be routinely measured by means of DSC (or DTA) scans, which also provide the temperature of onset of glass crystallization, T_x, as well as estimates of the solidus and liquidus temperatures of the system (which may vary with the scan rate).



Sakka and Mackenzie (1971) have established the so-called “two thirds” rule, which expresses the fact that, for most good glass-forming substances (or systems), the ratio between T_g and the melting (or liquidus) temperatures is of the order of “two thirds”:

$$T_g / T_m \sim 2/3$$

when the temperatures are expressed in Kelvin.

(For poor glass-forming systems, this ratio is often close to 0.60 or 0.70, rather than 0.66).