<u>**Optical and Photonic Glasses**</u>

Lecture 4:

Glass Composition and Preparations

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For a given, selected value of V (in fact, it makes little difference whether this is 10^{-6} or 10^{-8}, for example), the T-T-T curve is built by calculating, for each temperature in a range of interest, the time which a fraction V takes to crystallize at a temperature T (at which the nucleation and growth rates are I_v and u, respectively).

The "nose" of the curve, which has the coordinates (t_n, T_n), defines the **critical cooling rate**, $(dT/dt)_c$, as the *slope* of the line drawn between T_m and the "nose":

$$(dT/dt)_c \sim \Delta T_n / t_n$$

which means that, when the melt reaches T_n after a cooling time t_n ($\Delta T_n = T_m - T_n$), the crystallized fraction will not exceed the chosen value of V. Actual continuous cooling conditions correspond to lower real values of V and easier vitrification.

Another empirical criterion is: $$(dT/dt)_c \sim 10^5 / \eta_f \quad (^oC/s)$$

where η_f is the melt viscosity at T_m, in Pa.s .

Note that the "melting" temperature, T_m, may actually be well over T_L.

In general, **glass formation** will be favored by: (1) a cooling rate as high as possible; (2) a high viscosity at the nose of the T-T-T curve (and at T_m); (3) absence of heterogeneous nucleation sites; (4) a large liquid-crystal interfacial energy γ; (5) in multicomponent systems, a large compositional change between liquid and crystalline phase formed (in such systems, glass formation is also favored by a *deep eutectic*, at "low T", where the melt viscosity is higher).

Examples of Critical Cooling Rates (°C/s) for Glass Formation

Material	Homogeneous nucleation	Heterogeneous nucleation contact angle (deg) 100	60	40
SiO_2 glass[a]	9×10^{-6}	10^{-5}	8×10^{-3}	2×10^{-1}
GeO_2 glass[a]	3×10^{-3}	3×10^{3}	1	20
$Na_2O{\cdot}2SiO_2$ glass[a]	6×10^{-3}	8×10^{-3}	10	$3 \times 10^{+2}$
Salol	10			
Water	10^{7}			
Ag	10^{10}			
Typical metal[a]	9×10^{8}	9×10^{9}	10^{10}	5×10^{10}

[a] After P. I. K. Onorato and D. R. Uhlmann, J. Non-Cryst. Sol., 22(2), 367–378 (1976).

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

Glass composition and preparation

Commercial glass compositions are based on complex mixtures of *glass-forming* compounds, glass *modifiers* and *intermediates*, in the Zachariasen/Sun sense previously discussed.

Although most industrial glasses are based on the glass former SiO_2, many other compounds are normally added, whether also glass formers like B_2O_3, or other modifiers and intermediates.

We will start by considering the most important case, from an industrial viewpoint, of glasses prepared by cooling from the molten state.

Glass formers

A Partial List of Glasses Formed by Cooling from a Melt[a]

Elements
- S, Se
- Te(?)
- P

Oxides
- B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_3, Sb_2O_3
- In_2O_3, Tl_2O_3, SnO_2, PbO_2, SeO_2
- "Conditional" TeO_2, SeO_2, MoO_3, WO_3, Bi_2O_3, Al_2O_3, Ba_2O_3, V_2O_5, SO_3

Sulfides
- As_2S_3, Sb_2S_3
- various compounds of B, Ga, In, Te, Ge, Sn, N, P, Bi
- CS_2

Selenides
- various compounds of Tl, Sn, Pb, As, Sb, Bi, Si, P

Tellurides
- various compounds of Tl, Sn, Pb, As, Sb, Bi, Ge

Halides
- BeF_2, AlF_3, $ZNCl_3$, Ag(Cl, Br, I), Pb(Cl_2, Br_2, I_2), and multicomponent mixtures

Nitrates
- KNO_3—$Ca(NO_3)_2$ and many other binary mixtures containing alkali and alkaline earths nitrates

Sulfates
- $KHSO_4$ and other binary and ternary mixtures

Carbonates
- K_2CO_3—$MgCO_3$

Simple organic compounds
- *O*-Terphenyl, toluene, 3-methyl hexane, 2,3-dimethyl ketone, diethyl ether, isobutyl bromide, ethylene glycol, methyl alcohol, ethyl alcohol, glycerol, glucose
- As droplets only: *m*-xylene, cyclopentane, *n*-heptane, methylene chloride

Polymeric organic compounds
- Example—polyethylene ($-CH_2\cdot-$), and many others

Aqueous solutions
- Acids, bases, chlorides, nitrates, and others

Metallic alloys by "splat cooling"
- Au_4Si, Pd_4Si
- Te_x–Cu_{25}–Au_5

[a] After R. H. Doremus, *Glass Science*, p. 12. Wiley-Interscience, New York, 1973. Reproduced with permission of J. Wiley & Sons.

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

Abundance of chemical elements in earth crust (on a mol% basis):

O -	50 %
Si -	25 %
Al -	7 %
Fe -	4 %
Ca -	3 %
Na -	2.5 %
K -	2 %
Mg -	2 %
	95.5 %

Minerals:

silicates

alumino-silicates

other oxides

Typical oxide glass compositions (in weight %)

window: 72 SiO_2-1 Al_2O_3-10 CaO-2.6 MgO-13.6 Na_2O (soda-lime glass)

container: 72 SiO_2-2 Al_2O_3-10 CaO-0.8 K_2O-13.7 Na_2O …

borosilicate: 80 SiO_2-12 B_2O_3-2 Al_2O_3-5 Na_2O … ("pyrex glass",…)

fiber: 54 SiO_2-10 B_2O_3-14 Al_2O_3-17.5 CaO-4.5 MgO

optical: 46 SiO_2-45 PbO-7 K_2O-1.7 Na_2O …

Typical compositions of commercial glasses (wt %)

Glass	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	BaO	Na_2O	K_2O	SO_3	F_2	PbO	B_2O_3	ZnO	TiO_2	Cr_2O_3	As_2O_5	CeO_2
Flint container	72·6	1·6	0·05	11·0	0·1	—	13·7	0·5	0·2	—	—	—	—	0·1	—	—	—
Amber container	72·7	1·9	0·22	10·0	—	—	13·8	1·0	0·03	—	—	—	—	—	—	—	—
Green container	72·0	1·1	0·96	8·4	2·1	—	15·1	—	—	—	—	—	—	—	0·19	—	—
Flat	72·8	1·4	0·1	8·2	3·8	—	12·8	0·8	0·3	—	—	—	—	—	—	—	—
Borosilicate	80·2	2·6	0·07	0·1	—	—	4·5	0·3	—	—	—	12·3	—	—	—	—	—
Lighting ware (opal)	59·9	6·1	0·05	—	—	1·3	14·9	2·3	—	5·8	—	0·8	2·4	—	—	—	—
Full lead crystal	54·9	0·1	0·02	—	—	—	0·2	12·3	—	—	31·9	0·5	—	—	—	0·5	—
Lead crystal	58·5	—	0·02	—	—	—	1·3	13·1	—	—	25·2	1·5	—	—	—	0·5	—
Glass fibre, "A" glass	72·0	2·5	0·5	9·0	0·9	—	12·5	1·5	—	—	—	0·5	—	0·1	—	—	—
Glass fibre, "E" glass	55·2	14·8	0·3	17·7	4·3	—	0·3	0·2	—	0·3	—	7·3	—	—	—	—	—
Colour TV screen	63·2	3·3	—	1·8	1·1	12·7	9·9	7·5	—	—	—	—	—	—	—	—	0·21
Aluminosilicate	57·0	20·5	0·01	5·5	12·0	—	1·0	—	—	—	—	4·0	—	—	—	—	—
Light barium crown	57·1	0·2	—	0·3	—	26·9	—	13·7	—	—	—	1·8	—	—	—	—	—
Dense barium crown	36·2	3·5	—	0·2	—	44·6	—	0·2	—	—	—	7·7	—	—	—	—	—
Light flint	52·5	0·2	—	0·3	—	—	—	9·5	—	—	37·5	—	—	—	—	—	—
Dense flint	48·0	0·2	—	0·3	—	—	5·2	1·2	—	—	45·1	—	—	—	—	—	—

(Adapted from: Glass-making today, P.J. Doyle, Portcullis press, 1979)

Note: the term *flint* is normally used for glasses which contain significant amounts of PbO, including the so-called lead *crystal* glasses (24-32 wt% PbO) and the optical *flint* glasses, containing even higher amounts of PbO (light flint, with up to ~ 44 wt% PbO and dense flint, with up to ~ 60 wt% PbO); *crown* glasses usually have BaO or La_2O_3.

Raw materials

Name	Formula	Molecular weight	oxide
Boric acid	H_3BO_3	61·84	B_2O_3
Borax	$Na_2B_4O_7.10H_2O$	381·43	B_2O_3 Na_2O
Anhydrous borax	$Na_2B_4O_7$	201·27	B_2O_3 Na_2O
Limestone	$CaCO_3$	100·09	CaO
Dolomite, pearlspar	$MgCO_3.CaCO_3$	184·42	CaO MgO
Hydrated lime	$Ca(OH)_2$	74·10	CaO
Magnesite	$MgCO_3$	84·33	MgO
Barium carbonate, witherite	$BaCO_3$	197·37	BaO
Barium sulphate, barytes	$BaSO_4$	233·43	BaO SO_3
Red lead, minium	Pb_3O_4	685·43	PbO
Litharge	PbO	223·19	PbO
Soda ash	Na_2CO_3	106·00	Na_2O
Sodium sulphate, saltcake	Na_2SO_4	142·06	Na_2O SO_3
Sodium nitrate, chili-saltpetre	$NaNO_3$	85·01	Na_2O
Potash, pearl ash	K_2CO_3	138·21	K_2O
Glassmakers' potash	$K_2CO_3.1\frac{1}{2}H_2O$	165·24	K_2O
Potassium nitrate, saltpetre	KNO_3	101·10	K_2O
Lithium carbonate	Li_2CO_3	73·89	Li_2O
Fluorspar	CaF_2	78·08	CaO F_2
Cryolite	$AlF_3.3NaF$	209·97	Al_2O_3 Na_2O F_2
Sodium silico-fluoride, sodium fluosilicate	Na_2SiF_6	188·05	Na_2O SiO_2 F_2
Sodium fluoride	NaF	42·00	Na_2O F_2
Calcium sulphate, anhydrite, gypsum, finaglass	$CaSO_4$	136·15	CaO SO_3
Sodium chloride, salt	NaCl	58·45	Na_2O Cl_2

(Adapted from: Glass-making today, P.J. Doyle, Portcullis Press,1979)

Preparation of oxide glasses

A) Industrial scale

B) Laboratory scale

MAIN FAMILIES OF OXIDE GLASSES:

- silicates
- borates
- germanates
- phosphates

Fabrication methods

- **melting** (and casting: stones, striae, cords)
- **sol-gel** (and densification: cracking)
- **chemical vapor deposition** (CVD, and densification)
- **flame hydrolysis deposition** (FHD, and densification)
- **physical vapor deposition** (PVD: thermal or e-beam evaporation, sputtering, PLD)

Types of glass

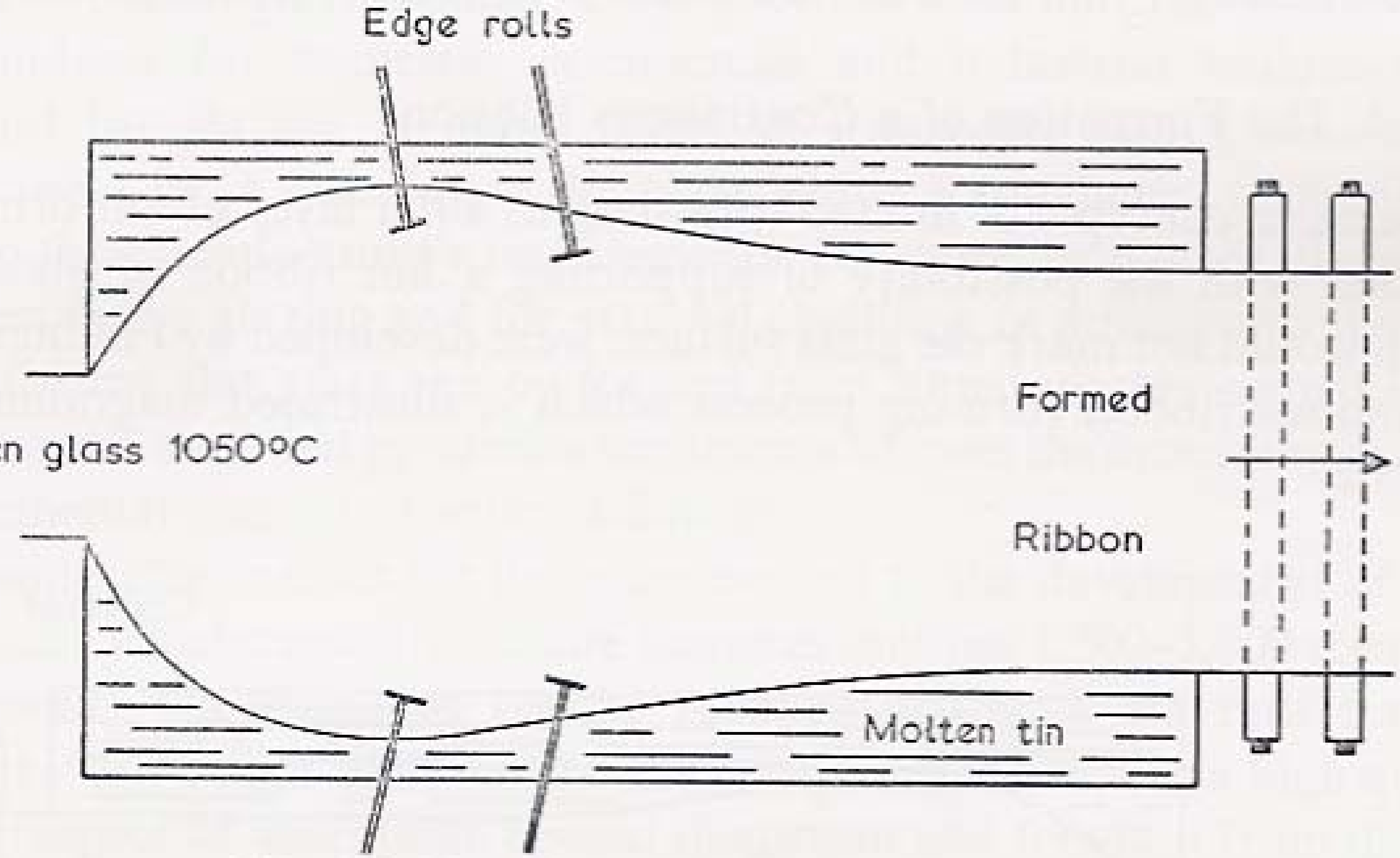
A) Flat glass (window)

- Horizontal draw (Libbey-Owens, 1905)
- Vertical draw (Fourcault, 1902; Pittsburgh, 1926)
- Float glass (Pilkington, 1965)

B) Hollow glass (container, tubing)

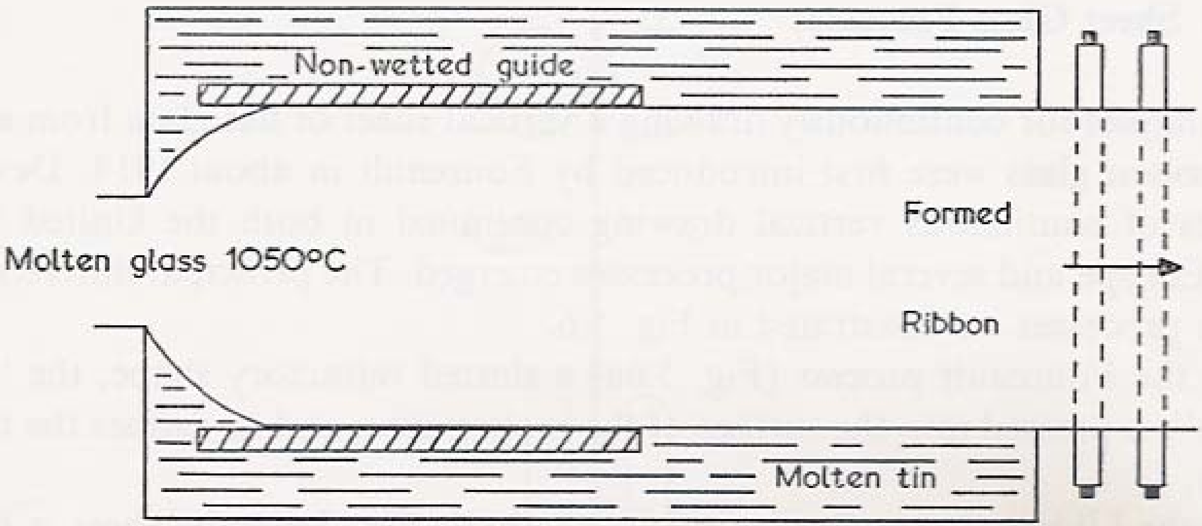
- Blowing
- Drawing (tubing)
- IS machines (bottles, …)

C) Fiber glass

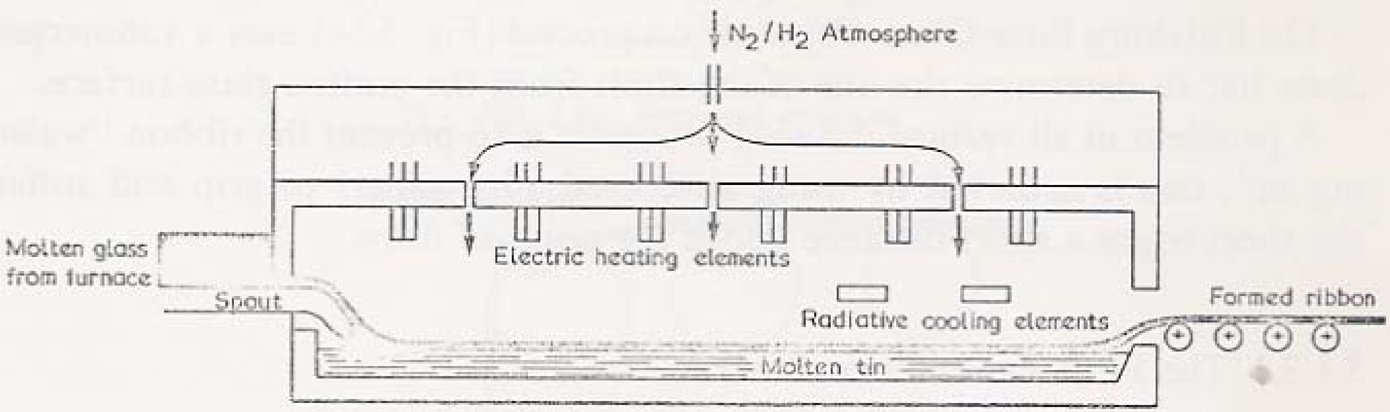


Manufacture of thin float ribbon (~ 2 – 10 mm)

(Adapted from: *Glass-making today*, P.J. Doyle, Portcullis press, 1979)



4. *Manufacture of thick float ribbon* (~ 10 – 25 mm)



5. *Vertical section through float bath*

Molten Sn bath in a N_2 / 10%H_2 reducing atmosphere.

(Adapted from: Glass-making today, P.J. Doyle, Portculis Press, 1979)

C) **Glass** fiber

- for insulation (sieve-like Pt bushing)
- continuous fiber (drawn from Pt bushing)
- optical fiber (high silica fibers)

Sol-gel glasses

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 19^{th} 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:

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

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.