Lecture 12:

Optical Glasses – Classification and Fabrication

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For New Functionality in Glass

Lehigh University

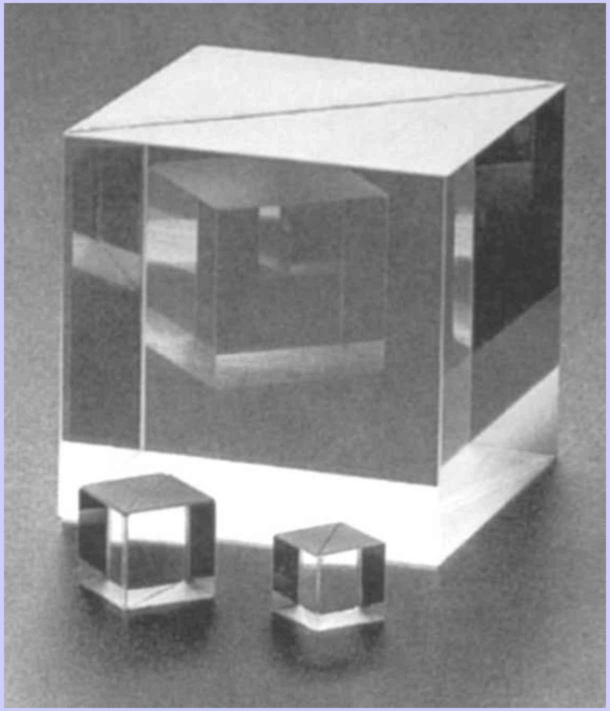
Optical glasses: fabrication and optical properties

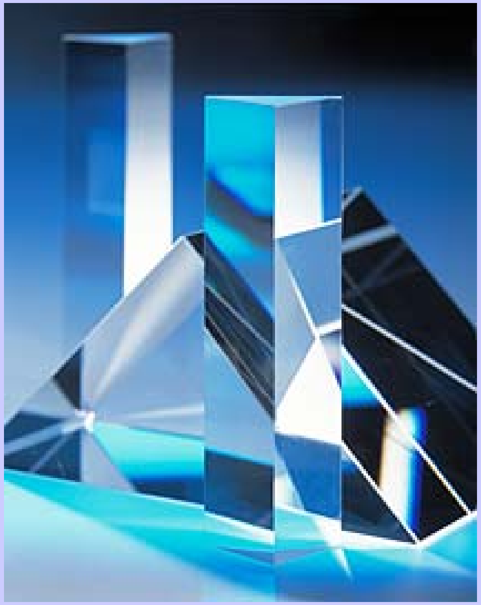
What is optical glass?

Optical glass is *optically homogeneous* glass, free from defects such as striae and bubbles, which is used with optical functionalities, for example in the form of lenses or prisms. The first optical quality (*flint*) glasses were developed by Otto Schott (in Jena, Germany), around 1890, who also invented Ba *crown* glass, enabling the fabrication of lenses corrected for chromatic aberration.

In 1939, G.W. Morey (in USA) invented an optical glass containing La, Th and Ta, possessing high refractive index and low dispersion.

After 1945, many new optical glass compositions were developed, together with improved manufacturing methods, by T. Izumitani and other japanese researchers, first in Osaka and later at the Hoya Glass corporation (Tokyo, Japan).

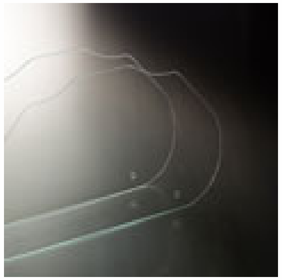




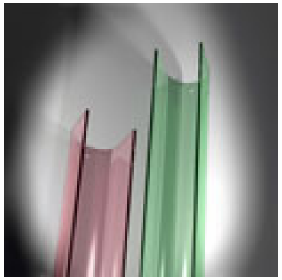
Mirrored glass
Mirrored glass with chrome coating.

UVILEX® 390 Z
UV-barrier filter glass that reduces ultraviolet radiation from artificial light sources.

Borofloat®
Glass with high chemical resistance, low thermal expansion and high temperature resistance.



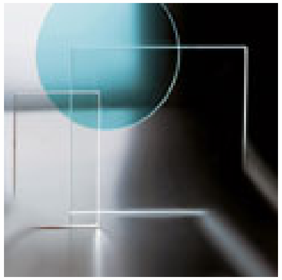
CONTURAN®
Optical interference anti-reflective glass, dip-coated on both sides, with various transmittances. Eliminates most irritating reflections.



Coloured glass
Machine drawn coloured glass with smooth (IMERA) and structured

(ARTISTA®) surfaces in a wide range of colours.

B 270 Superwite
Highly transparent, low iron glass. Cylindrical in form with silkscreen printing or inside laser structure for use in technical lighting applications.



Filter glass
Blue-violet tinted filter glasses with variously specified UV transmittance and high absorption in the visible and infrared range, as well as clear filters with graded UV transmittances. All

(Adapted from: www.us.schott.com)

Traditional optical glasses – composition and fabrication

The compositions of the more traditional optical glasses are usually based on multi-component silicates, including heavy elements such as Pb, Ba, La, Gd, Ta and Nb. The basic compositions usually fall into two categories: (1) high dispersion *flint* glasses (normally containing PbO); (2) low dispersion *crown* glasses (often containing Ba or La).

Principal components of optical glasses.

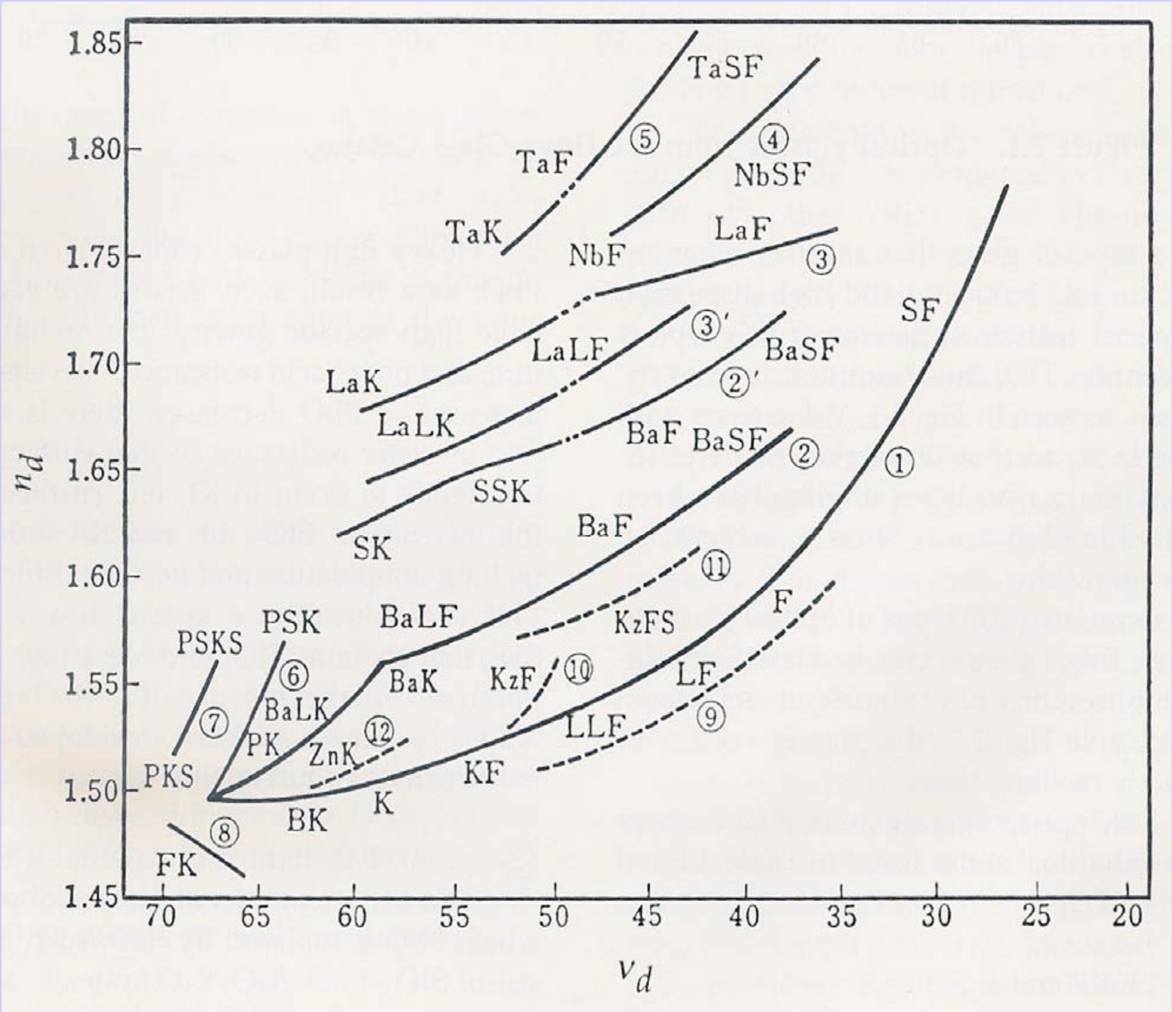
Series	Flint	Crown
(1)	SiO_2–PbO–R_2O	→SiO_2–RO–R_2O
(2)	SiO_2–PbO–BaO–R_2O	→SiO_2–BaO–R_2O
(2)′	SiO_2–B_2O_3–PbO–BaO	→SiO_2–B_2O_3–BaO
(3)	(SiO_2)–B_2O_3–La_2O_3–PbO–Al_2O_3	→(SiO_2)–B_2O_3–La_2O_3–RO–ZrO_2
(3)′	(SiO_2)–B_2O_3–La_2O_3–PbO–RO	→(SiO_2)–B_2O_3–La_2O_3–RO–ZrO_2
(4)	(SiO_2)–B_2O_3–La_2O_3–ZnO–TiO_2–ZrO_2	→(SiO_2)–B_2O_3–La_2O_3–ZnO–Nb_2O_5
(5)	B_2O_3–La_2O_3–Gd_2O_3–Y_2O_3–Ta_2O_5	→B_2O_3–La_2O_3–Gd_2O_3–Y_2O_3
(6)		SiO_2–B_2O_3–R_2O–BaO
(7)		P_2O_5–(Al_2O_3–B_2O_3)–R_2O–BaO
(8)		SiO_2–B_2O_3–K_2O–KF
(9)	SiO_2–TiO_2–KF	
(10)	SiO_2–B_2O_3–R_2O–Sb_2O_3	
(11)	B_2O_3–(Al_2O_3)–PbO–RO	
(12)		SiO_2–R_2O–ZnO

(Adapted from: *Optical glass*, T.S. Izumitani, Hoya Corp. / Amer. Inst. Physics, 1986)

Such optical glass series can be conveniently represented on a plot of the *refractive index* (e.g. n_d, the glass refractive index for the **d** line of He at 587.6 nm, or n_D, the index for the **D** line of Na at 589.3 nm) as a function of *dispersion* (or the change in index with the wavelength of light, usually represented by the *reciprocal dispersion* or Abbe number, $\nu_d = (n_d-1)/(n_F-n_C)$, with F and C corresponding to the **F** and **C** lines of hydrogen, at 486.1 nm and 656.3 nm, respectively). The refractive index difference (n_F-n_C) is called the *mean dispersion*.

In this terminology, *flint* glasses are optical glasses with **high dispersion** (ν_d < 50-55), whereas *crown* glasses are those with **low dispersion** (ν_d > 50-55).

The general tendency is for the optical glasses to follow a curve going from the lower left corner of *fluor-crowns*, typically low index/low dispersion borosilicates with F or P, to the upper right corner of high index/high dispersion *heavy flint* glasses, with high PbO and/or La_2O_3 contents.



Classification of the optical glass series.

(Adapted from: *Optical Glass*, T.S. Izumitani, Hoya Corp. / Amer. Inst. Physics., 1986)

In addition to the *flint* and *crown* designations (*flint* glasses with names ending with **F** and *crown* glasses ending with **K**), there are subdivisions, namely: **BK** (for low Ba *borosilicate crown*, e.g. BK7, the most common optical glass), **SK** (for high Ba, *heavy borosilicate crown)*, **KF, LF, F, SF** (for *flint* glasses with increasing PbO contents, from *light* to *heavy*) and **P, F, K (**for glasses containing phosphorus, fluorine and potassium, respectively).

Compositions of optical glasses (wt%).

	SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	CaO	ZnO	BaO	PbO	Sb_2O_3	As_2O_3	KHF_2	TiO_2	P_2O_5
SF 2	40.9			0.5	6.8				50.8		1.0			
SF 6	26.9			0.5	1.0				71.3		0.3			
F 2	45.7			3.6	5.0				45.1		0.6			
F 8	50.2			3.8	5.6				39.7		0.3			
LF 1	54.3			4.4	7.8		1.0	1.5	34.9		0.8			
LF 7	33.9			2.5	7.9				45.1		0.6			
KF 2	66.7			15.9			3.5		12.9		1.0			
K 8	70.7	2.8		5.8	11.3			6.4	2.8		0.4			
BaSF 2	23.6	10.5	1.5			7.0	5.9	29.3	14.2	0.4	0.6		7.0	
BaF 10	30.9	9.2	0.3			4.0	5.3	41.3	4.6		0.3		3.6	
BaLF 1	53.8			1.5	9.5		10.0	14.2	10.7		0.3			
BaK 1	47.7	4.2	1.0	1.0	7.5		8.6	29.0			0.2			
BaK 2	59.6	3.0		3.0	10.0		4.8	19.0			0.6			
SSK 2	37.3	6.3	2.5				8.0	39.7	5.2		1.0			
SK 1	40.1	5.7	2.5				8.5	42.2	0.5		0.5			
SK 3	35.0	11.9	4.5					45.9	0.6	1.6	1.0			
SK 5	38.7	14.9	5.0					40.1		0.3	1.0			
SK 16	30.8	17.9	1.4	0.3				48.7		0.4	0.5			
PK 1	68.2	13.5	1.3		12.1		0.5	3.0				2.4		
BK 1	71.4	6.5		5.2	13.9	2.0					1.0			
BK 7	68.9	10.1		8.8	8.4		MgO	2.8			1.0			
PKS 1		4.0	9.0		11.6		4.0				1.0			70.4
FK 1	51.0	18.3	8.3		7.3						0.2	14.4		
FK 3	47.7	17.4	1.4	2.2	2.4						0.3	16.0		
KzF 1	46.0	14.0	3.0		12.0		4.0			20.6	0.4			
ZK 1	55.7	7.0		1.0	16.0		20.0				0.3			

	SiO_2	B_2O_3	La_2O_3	ZrO_2	CaO	BaO	PbO
LaF 2	4	32.7	29.0	7.5	11.0		15.8
LaF 3	4	37.3	25.7	7.4	10.7	4.0	10.7
LaK 10		41.3	32.4	8.1	12.1		6.1

Pb flints (Pb, or Pb/Ba silicates)

Ba crowns (borosilicates)

K crowns (borosilicates)

La flints (La/Pb borates)

(Adapted from: *Optical Glass*, T.S. Izumitani, Hoya Corp. / Amer. Inst. Physics, 1986)

Physical and chemical characteristics of optical glasses.[a,b]

	n_d	ν_d	Thermal properties Sp (°C)	$\alpha \times 10^7$ (°C^{-1})	Chemical durability[c] Da	Dw
SF 2	1.64769	33.9	483	98	3	2
→ SF 6	1.80518	25.5	480	85	4	2
F 2	1.62004	36.3	454	101	1	2
F 8	1.59551	39.2	481	85	1	1
LF 1	1.57309	42.7	471	99	1	2
LF 7	1.57501	41.3	471	94	1	2
KF 2	1.52630	51.0	514	94	1	2
K 8	1.51276	59.8	542	88	1	3
BaSF 2	1.66446	35.9	536	85	3	2
BaF 10	1.67003	47.2	671	82	4	2
BaLF 1						
BaK 1	1.57250	57.5	639	80	4	1
BaK 2	1.53996	59.7	618	83	1	2
SSK 2	1.62230	53.1	680	74	5a[d]	2
SK 1	1.61025	56.5	680	76	4	2
SK 3	1.60881	58.9	689	76	5a[d]	2
SK 5	1.58913	61.2	680	72	4	2
SK 16	1.62041	60.3	672	75	5b[d]	3
PK 1						
BK 1	1.51009	63.4	610	92	1	2
→ BK 7	1.51680	64.2	642	88	1	1
PKS 1	1.51728	69.6	545	80	2	5
FK 1	1.47069	67.2	492	87	4	2
→ FK 3	1.46450	65.8	475	87	4	2
KzF 1	1.55115	49.6	525	71	4	2
ZK 1	1.53315	58.1	592	78	4	2
LaF 2	1.74400	44.9	584	77	5a	2
LaF 3	1.71700	47.9	668	93	5a	1
→ LaK 10	1.72000	50.3	650	74	5a	2

Grade	Da 1	Da 2	Da 3	Da 4	Da 5
Weight reduction (%)	<0.03	0.03 to 0.10	0.10 to 0.30	0.30 to 1.00	>1.00

Grade	Dw 1	Dw 2	Dw 3	Dw 4
Weight reduction (%)	<0.05	0.05 to 0.20	0.20 to 0.50	0.50 to 1.00

[a] Acid resistance was measured by immersing specimens for 1 hour at 50°C in 150 ml of 1/100 N HNO_3; the specimens were classified according to percentage of weight reduction.

[b] Durability was measured by boiling the coarsely pulverized glass for a fixed period of time in a fixed amount of distilled water, and then measuring the weight reduction (%).

(Adapted from: *Optical Glass*, T.S. Izumitani, Hoya Corp. / Amer. Inst. Physics, 1986)

Physical–chemical properties of glass.

Glass type	Softening point (°C)	Vickers hardness (kg/mm^2)	Acid-resistance weight loss (%)	Water-resistance weight loss (%)
→ BK 7	615	707	0.08	0.13
KF 2	490	627	0.07	0.07
SK 2	700	707	0.70	0.05
SK 16	680	689	3.3	0.58
→ SF 6	470	413	1.3	0.03
→ FK 1	475	666	1.9	—
SF 13	480	437	0.34	0.02
KF 3	500	627	0.04	0.05
BaF 4	580	613	0.11	0.04
BaK 4	620	657	0.43	—
F 3	480	548	—	—
LaKF 2	675	803	1.3	0.25
→ LaK 12	670	743	1.7	0.35
LaLK 13	650	762	1.9	0.70
NbF 1	650	824	1.0	0.01
TaF 2	685	847	0.74	0.01
LaK 10	670	803	1.2	0.02
NbSF 3	650	803	0.76	0.01

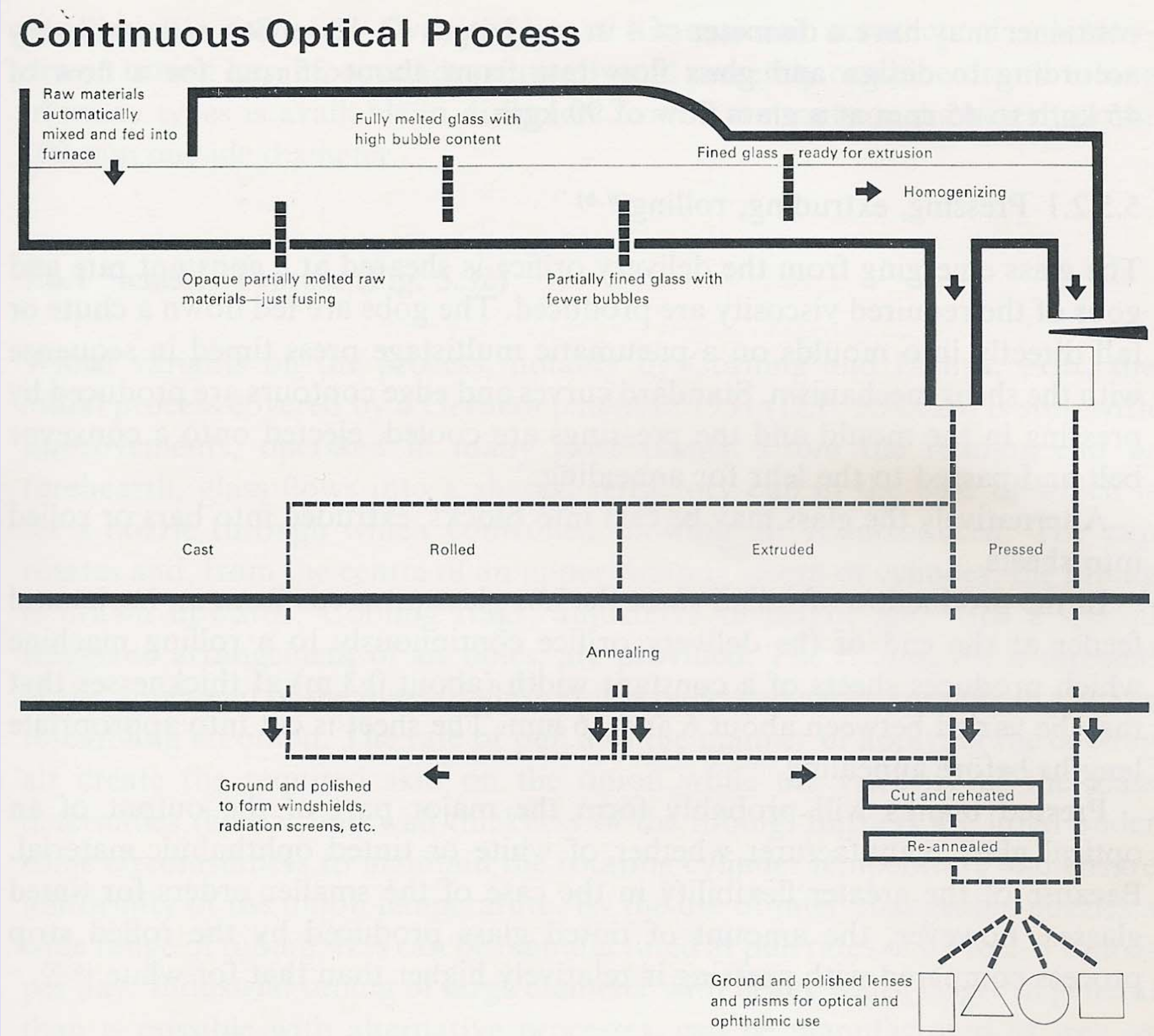
(Adapted from: *Optical Glass*, T.S. Izumitani, Hoya Corp. / Amer. Inst. Physics, 1986)

Fabrication of traditional optical glasses

Clay pot melting, introduced by Schott in Germany, was the first method used to melt optical glass. However, the melts caused erosion of the clay, which led to striae in the final glass and they also became contaminated by iron and very fine (~ micron sized) bubbles (sometimes called "seeds") generated by the porous clay. Stirring of the melts was usually insufficient to prevent the formation of striae.

The appearance of La borate glasses in 1945, containing very little SiO_2 and therefore with rather low viscosity, led to a switch from clay to platinum pots, with a consequent remarkable reduction in striae and bubbles and a corresponding improvement in the quality of optical glass. The melting yield was also significantly raised, from ~ 40% to ~ 80%. In addition, the stirring speed could be raised, in order to further eliminate striae, without a simultaneous formation of bubbles.

Nevertheless, the use of platinum pots in a *batch* process where these had to be withdrawn from the furnace after melting and left cooling for several days (during which cracking occurred) prevented efficient mass production of the optical glass. The third revolution in the manufacturing of optical glass occurred between 1960-1965, with the introduction of *continuous melting* process, similar to those used for plate or bottle glass, in USA (Bausch & Lomb and Corning) and particularly in Japan (Hoya Glass).



. The bubble free glass may be cast into blocks, rolled into sheets, extruded into bars, or pressed into blanks. After careful annealing it may be further processed by remoulding, grinding and polishing

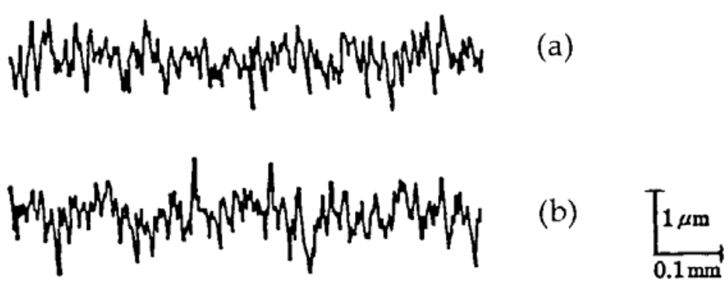
(Adapted from: *Glass-making today*, P.J. Doyle, Portculis Press, 1979)

In the continuous melting process, melting of the glass takes place in a small tank furnace, with raw material feeding, melting, stirring and fining taking place in separate sections of the tank. Platinum is normally used as the contact material between the molten glass and refractory. Although the initial zone of the furnace is fuel-fired, electric melting is used in the finishing stage. Melting yields of up to ~ 90% are thus possible to achieve. All-electric melting is also common nowadays, due to improved thermal efficiency.

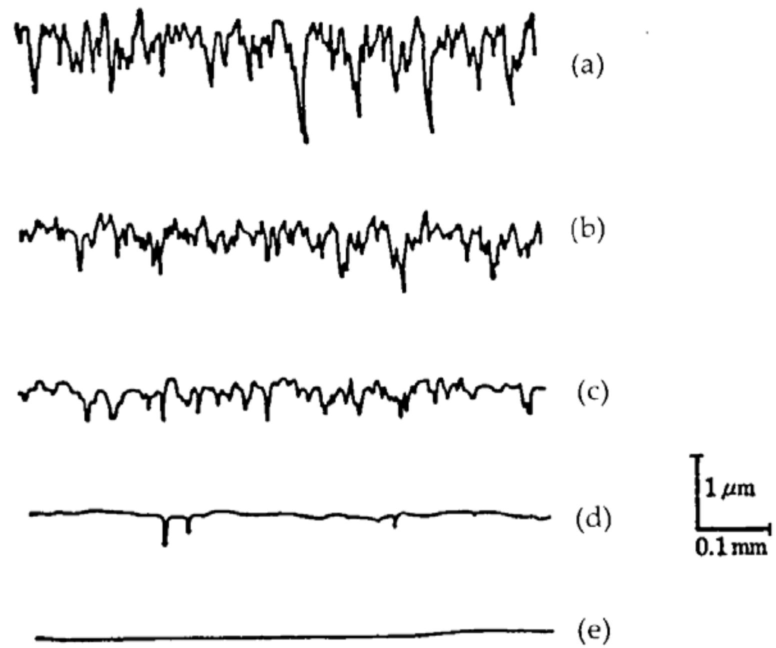
The glass emerging from the tank may be cast into **blocks**, extruded into **bars**, or rolled into **sheets**, followed by careful **annealing**, an essential step to ensure the glass homogeneity (e.g. with a refractive index constant throughout the glass up to the 5^{th} decimal figure). Alternatively, the glass emerges from a delivery orifice in the form of gobs which fall into molds, where they are pressed, cooled, ejected and then passed to the lehr for annealing.

Pressed blanks, which usually form the major part of the output of an optical glass manufacturer, finally undergo cold working consisting of **grinding (**diamond), lapping (smoothing with free abrasive particles) and **polishing** into lenses or prisms.

Polishing is normally performed with **cerium oxide** spread on a pad, causing the formation of a soft, hydrated layer on the glass surface, until a mirror finish is obtained. The polishing rate is found to be inversely proportional to the hardness of the hydrated surface layer. The glass chemical durability will determine the ease with which a hydrated layer is formed.



Changes in surface roughness in polishing with water only: (a) lapped surface and (b) 6 hr of polishing.



Changes in surface roughness in polishing with cerium oxide and water: (a) lapped surface, (b) 3 min of polishing, (c) 6 min of polishing, (d) 10 min of polishing, and (e) 15 min of polishing.

(Adapted from: *Optical Glass*, T.S. Izumitani, Hoya Corp. / Amer. Inst. Physics, 1986)