Optical and Photonic Glasses

Lecture 21:
Abnormal Dispersion and Athermal Glasses

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Abnormal dispersion and athermal glasses

Besides new optical glasses like the halides (fluorides) and chalcogenides, in the area of oxide glasses there have also been new developments.

In high dispersion (*flint*) glasses, traditionally containing large amounts of PbO, attempts have been made to replace PbO with compounds such as TiO_2 and Nb_2O_5, in order to decrease toxicity and increase hardness and chemical durability.

In low dispersion (*crown*) glasses, new fluorophosphate glass compositions have been developed, such as P_2O_5-AlF_3-RF_2-RF (where R represents an alkaline earth or alkali metal), which also show *abnormal dispersion* in the short wavelength region, as described below.

Borosilicate glasses with simultaneously high index and low density, containing Li_2O, TiO_2 and Nb_2O_5, have also been developed.

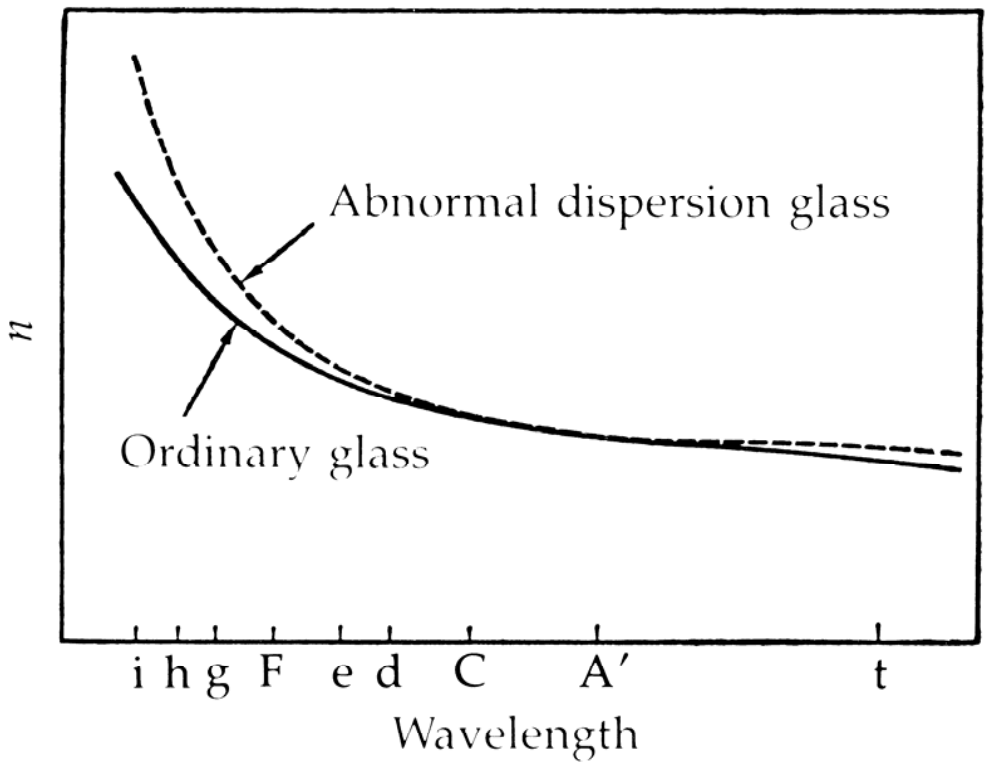
The chemical durability of certain optical glasses has also been improved by additions of La_2O_3 and ZrO_2, whereas index raising compounds like La_2O_3 and Nb_2O_5 have been increasingly used to replace more expensive raw materials like Ta_2O_5, which is at present in great demand as a source of Ta for capacitors in mobile telecommunications units.

The main factor which reduces image quality of an objective lens is the double dependence of its parameters on *wavelength* and *temperature*. Thus, in addition to spherical aberrations, both chromatic and temperature aberrations need to be carefully corrected in high performance optical systems. For example, the simple use of higher index glasses will reduce spherical aberrations in lenses, whereas the use of low dispersion glasses reduces color aberration. The so-called *apochromat* objectives, e.g., provide a good degree of simultaneous spherical and chromatic aberration correction, but, since they normally consist of two or three different lenses stacked together, they tend to exhibit secondary chromatic aberrations, due to the differences in dispersion between the different lens glasses (or materials) involved.

Secondary color chromatic aberrations in lens doublets or triplets may be conveniently controlled by optical glasses with anomalous relative partial dispersion, P, characterized by a dispersion coefficient (or Abbe number, ν_i) which departs from the normal straight line on a $P = f(\nu_i)$ diagram.

Temperature aberrations reduce the image quality even more strongly than primary chromatic and secondary color aberrations. These temperature effects may be minimized through the use of athermal glasses.

Abnormal dispersion glasses are glasses whose refractive index vs. wavelength curves differ from those of ordinary optical glasses, both at short and long wavelengths, as shown below. The wavelengths indicated are used to define the partial dispersion ratios: $P_{i,g} = (n_i - n_g)/(n_F - n_C)$, at short λ and $P_{C,t} = (n_C - n_t)/(n_F - n_C)$, at long λ values.

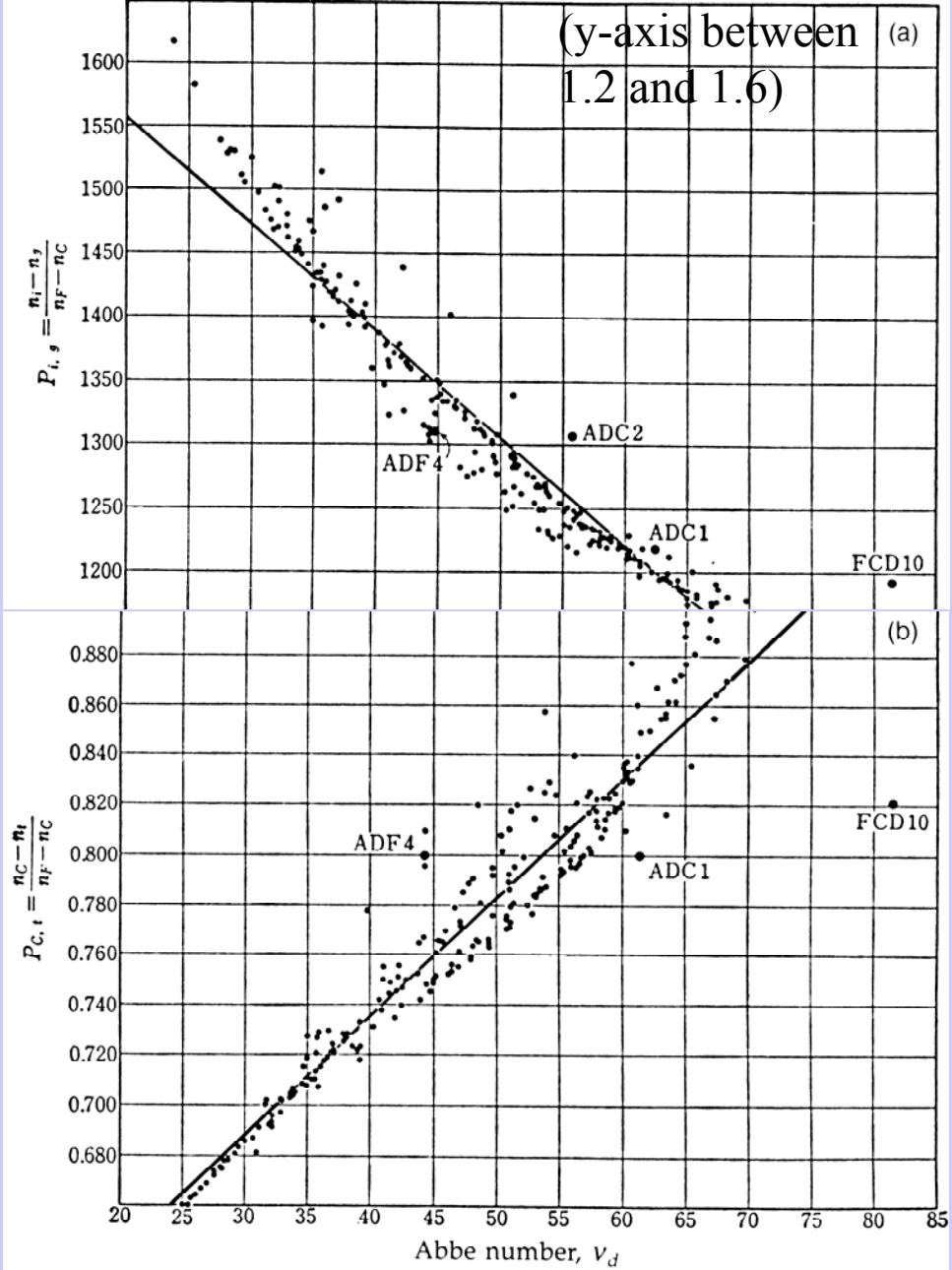


Abnormal dispersion characteristics seen in the wavelength dependence of the index of refraction.

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

For ordinary optical glasses, the relationship between the partial dispersion ratios and the Abbe number is roughly linear. Abnormal dispersion (AD) glasses deviate considerably from this linear behavior and are quite useful for the correction of chromatic aberration in lenses.

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



Relationship between partial dispersion and the Abbe number: (a) short wavelengths and (b) long wavelengths.

Explanation for abnormal dispersion

According to T. Izumitani, the reason for the pronounced abnormal dispersion characteristics of a fluorophosphate glass like FCD 10, e.g. (in the previous figure), is that it is a glass with a large content of F^- ions and therefore with stronger ionic character than conventional silicates, which thus exhibits electronic UV absorption at shorter wavelengths, whereas the onset of vibrational IR absorption occurs at longer wavelengths than silicate glasses.

However, this explanation does not seem to hold for other types of abnormal dispersion glasses.

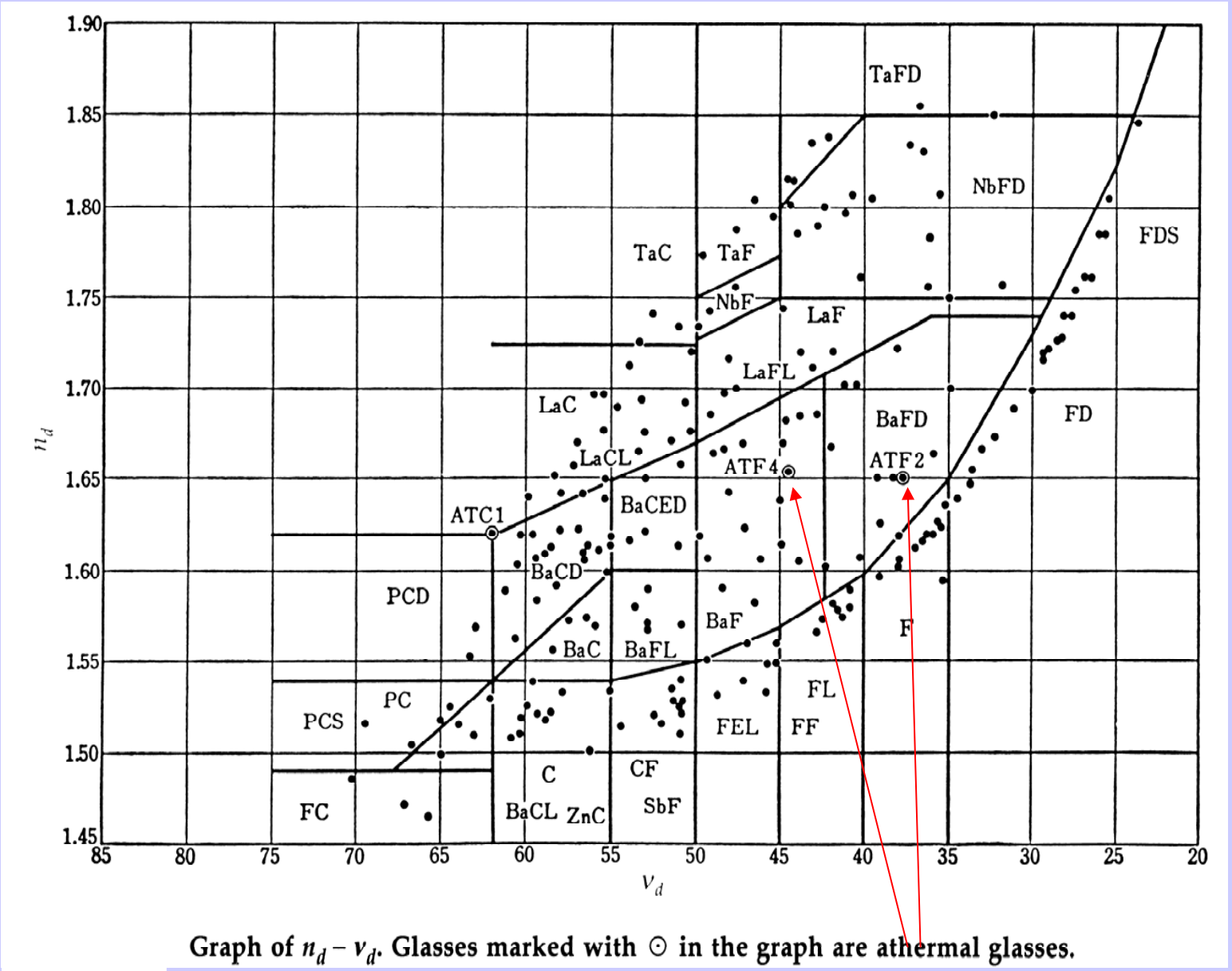
Athermal glasses

Athermal glasses are glasses in which the temperature coefficient of the light path length in the glass is zero. For example, the *focal length* of a lens made of an athermal glass will *not vary with temperature*. This can be rather useful in laser oscillators and telescopes in artificial satellites, for example.

The light path length, S, will change with temperature as a combined result of thermal expansion and temperature variation of the refractive index, which can be shown to be:

$$dS/dT = (n - 1)\,\alpha_T + dn/dT$$

For dS/dT to be zero, **dn/dT must be negative**.



Graph of $n_d - \nu_d$. Glasses marked with ⊙ in the graph are athermal glasses.

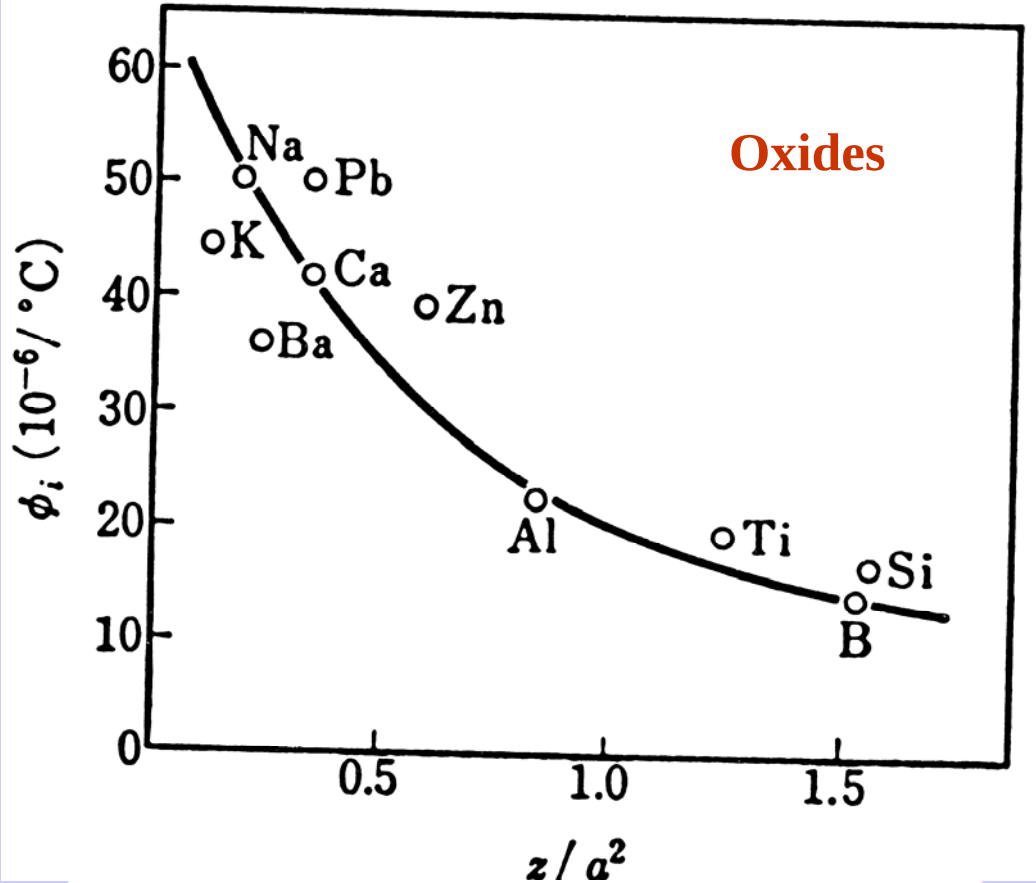
(Adapted from: *Optical glass*, T.S. Izumitani, Amer. Inst. Phys./Hoya Corp., 1986)

From the Lorentz-Lorenz (or Clausius-Mossotti) equation, the value of dn/dT can easily be calculated:

$$dn/dT = (n^2-1)(n^2+2) / 6n \, (d\ln\alpha_e/dT - 3\alpha_T)$$

where α_e is the electronic polarizability, which must increase with an increase in the interionic distances. In an athermal glass, the change in polarizability accompanying an increase in interatomic distances with temperature is smaller than the thermal expansion and causes dn/dT to be negative.

The temperature coefficient of α_e is related to the cationic field strength, $z_c / (r_c + r_a)^2$, decreasing with an increase in field strength, due to the fact that cations with higher field strength will polarize more strongly the electrons in the glass, making the electronic clouds simultaneously less polarizable.



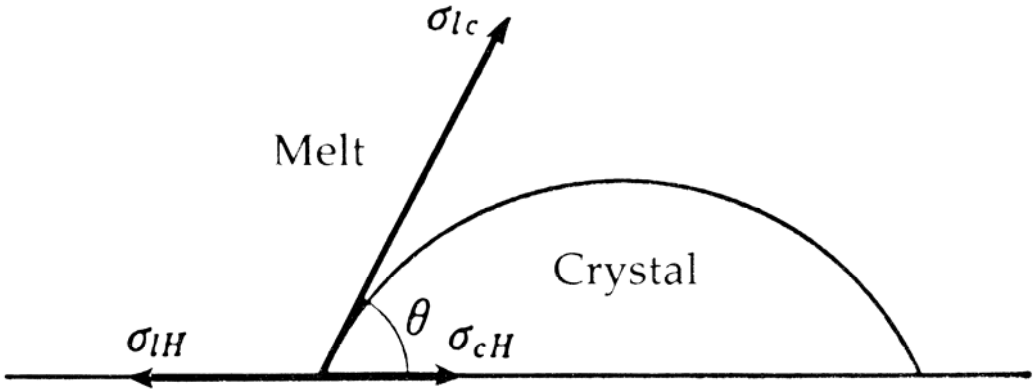
Relationship between cationic field strength (z/a^2) and temperature coefficient of electron polarizability (ϕ_i) of ions.

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

Transparent glass ceramics (TGC)

Glass-ceramics were invented by S.D. Stookey in 1959, by adding TiO_2 as a nucleating agent to a Li_2O-Al_2O_3-SiO_2 glass. In this case, it was later shown that the heterogeneous sites for *volume nucleation* of the major crystaline phase (β-quartz solid solution) consisted of pyrochlore [$Al_2(Ti_mZr_n)_2O_7$] nanocrystals (~ 2-3 nm dia) when 2% of both TiO_2 and ZrO_2 were added , but other researchers have argued that such sites might be liquid micro-droplets formed by glass-in-glass phase separation.

T. Izumitani has argued that the crystalline sites are more favorable for nucleation of the major crystalline phase, since the (scl) melt will wet a crystal surface more than a liquid droplet interface.



Heterogeneous nucleation at an interface.

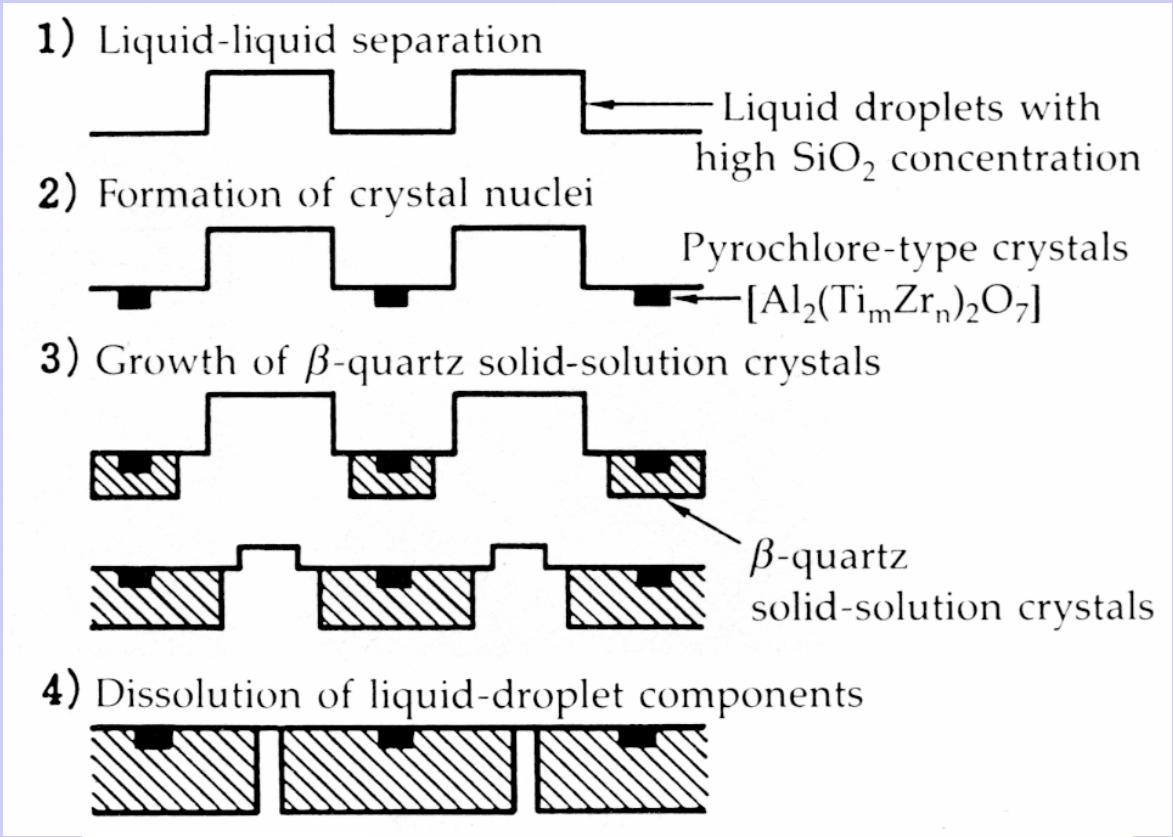
(Adapted from: *Optical glass*, T.S. Izumitani, Amer. Inst. Phys./Hoya Corp., 1986)

Mechanism of Crystallization

The question as to whether phase separation must precede crystallization in the preparation of GC is still the object of significant controversy. Nakagawa and Izumitani (1969) sustained that phase separation and crystallization are two unrelated, independent phenomena and that a liquid-liquid interface does not promote heterogeneous nucleation.

However, in a 75% SiO_2-20.5%Al_2O_3-4.5% Li_2O glass to which 2% TiO_2 and 2% ZrO_2 (in weight %) were added as nucleating agents, Doherty et al. (1967) found that, upon heat treatment of the originally homogeneous glass, the first phenomenon to occur was liquid-liquid phase separation into high silica liquid droplets, followed by the formation of pyrochlore-type crystals ~ 2-3 nm in size, made possible by the previous phase separation, which subsequently act as heterogeneous nucleation sites for β-quartz SS (where some Si^{4+} ions are replaced by Li^{+} and Al^{3+}), as shown in the next figure. So far, only droplet-like phase separation has been shown to lead to TGC, whereas spinodal decomposition usually leads to loss of glass transparency.

Crystallization Process



Formation process of SiO_2–Li_2O–Al_2O_3 crystallized glass with added TiO_2 and ZrO_2.

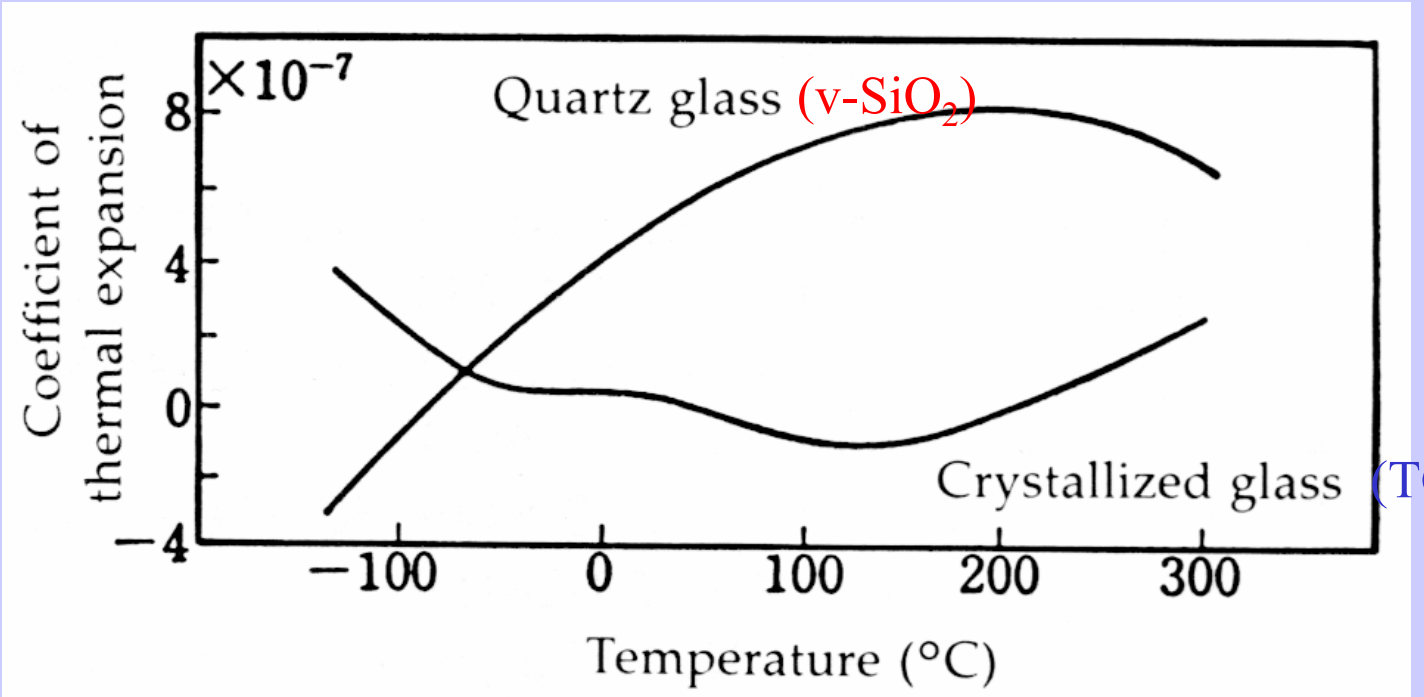
(Adapted from: *Optical glass*, T.S. Izumitani, Amer. Inst. Phys./Hoya Corp., 1986)

This Li aluminosilicate is an example of a TGC, containing ~ 80% of β-quartz SS nanocrystals ~ 20-40 nm in size, plus ~ 20% glassy phase. It is transparent because the average crystal size is < λ/10, for visible light.

Electron micrograph of SiO_2–Li_2O–Al_2O_3 crystallized glass containing TiO_2 and ZrO_2.

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

One very important property of this TGC is that its thermal expansion coefficient is close to zero, due to the fact that β-quartz SS has actually a slightly negative expansion coefficient , which approximately cancels out the positive expansion coefficient of the remaining glassy matrix. One practical example is the Zerodur GC (Schott), with 70% of 50 nm β-quartz crystal phase, $\alpha_T = 0 \pm 0.2 \times 10^{-7}\ K^{-1}$ between 0-100 ºC and ~ 90% transmittance between 0.6 – 2.0 μm.



Coefficients of thermal expansion of quartz glass and SiO_2–Li_2O–Al_2O_3 crystallized glass.

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

Characteristics of abnormal partial dispersion glasses compared with those of ordinary glasses.

	λ_0	KN_0f_0	λ_1	KN_1f_1	λ_2	KN_2f_2	λ_3	KN_3f_3	λ_4	KN_4f_4	n_d	ν_d	$P_{i,g}$	$P_{C,t}$
ADC 1	0.0634	225.13	0.127	40.85	0.155	0.790	—	—	10.0	0.00793	1.62000	62.19	1.2268	0.7955
BK 6	0.0684	166.29	0.108	18.20	0.175	0.509	—	—	9.7	0.00934	1.53113	62.15	1.2019	0.8500
			0.124	14.09										
			0.141	4.52										
ADC 2	0.0634	228.32	0.127	32.10	0.155	0.660	0.234	0.687	10.0	0.01013	1.59700	55.29	1.3126	0.8022
			0.139	1.00										
K 10	0.0684	143.09	0.106	18.83	0.172	2.095	0.196	0.140	9.8	0.00832	1.50137	56.41	1.2463	0.8213
			0.122	18.00			0.237	0.088						
ADF 4	0.0684	201.07	0.111	3.01	0.172	3.188	0.180	1.899	7.7	0.01298	1.61250	44.87	1.3237	0.8002
			0.139	20.02			0.238	0.468						
LLF 4	0.0684	150.70	0.106	18.71	0.175	5.883	0.199	0.389	9.8	0.00836	1.56138	45.23	1.3398	0.7608
			0.122	17.50			0.242	0.304						

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