Optical Glass

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VIII. Optical Properties of Glass

From ancient times to the present day the ***Transparency*** and ***Color*** of glasses have remained perhaps their most attractive physical properties. The successful utilization of glasses for optical applications, such as windows, lenses, containers, filters, lasers and waveguides often depends on the precise control of material transparency in a selected wavelength interval, and hence a thorough knowledge of optical properties and a good understanding of absorption process.

Since the optical properties of glasses are closely tied to the glass structure and composition, stress has been placed on relating the chemical bonding, symmetry, and coordination within the glass network to the observed optical properties.

The most characteristic property of glass is the transparency. This unique characteristic property of glass can lead the recent development of optical fibers or optical waveguides.

- SiO_2 optical fiber : 0.16dB / Km at 1.55μm

$0.16dB = 0.016 O.D. = Log(100/96.3)$

$$I_o = 100 \xrightarrow[\text{1Km}]{} I = 96.3$$

In general, an optical properties of glass deals with VUV(Vacuum Ultra Violet) to FIR(Far Infra Red) region. The wavelength ranges from about 10 nm to 300μm.

•VUV(Vacuum Ultra Violet) : 10 – 180 nm
•UV(Ultra Violet) : 180 – 380 nm
•Visible : 380 – 700 nm
•IR (Infra Red) : 700 nm – 30 μm
•FIR(Far Infra Red) : 30 μm – 300 μm

Optical properties of glasses can be divided into three main categories.

① Refractive Index and Dispersion
  (Bulk Optical Properties)
  Optical Glasses
② Absorption
  ● Intrinsic Absorption
    UV Absorption(Electronic Transition)
    IR Absorption(Vibrational, Rotational Transition)
    UV transmitting window,
    IR transmitting window(Optical waveguide in IR

region)

- ● Impurity Coloration: Visible region
  Electronic Transition
  - Transition Metal Ions(Fe^{2+}, Co^{2+}, Ni^{2+}, etc.)
  - Rare-Earth Ions(Nd, Pr, Er, etc.)
  - Metal Particles, Semiconductor Particles
    (Au, Ag, Cu, Cu_2O, CdS, CdS·Se, Se, S, etc.)
  - Amber Glass(Fe-S bond)
    Colored Glasses, Filters, Containers, Lasers, etc.

③ Opt-Magnetic, Opt-Acoustic, Lasers, Optical Fibers, Optical Waveguids, Photonics Devices

- ● Many researches are being done vigorously in this field.

1. Units and Nomenclature

Unfortunately, the units chosen by various authors differ. Usually, the visible region is ranging from 400 to700 nm. And energy units used in the optical spectroscopy is shown below.

	Cm^{-1}	EV	Erg
cm^{-1}	1	1.24×10^{-4}	1.99×10^{-16}
EV	8,066	1	1.60×10^{-12}
Erg	5.03×10^{15}	6.24×10^{11}	1

λ(nm) = 1,239.8 / eV : Wavelength
$\nu(cm^{-1}) = 1 / \lambda(cm)$: Wavenumber

Commonly, the following units are used in each region.

•UV Region : eV(Photon Energy), nm(wavelength)
•Visible Region : nm(wavelength), cm^{-1}(wavenumber)
•IR Region : μm(wavelength), cm^{-1}(wavenumber)

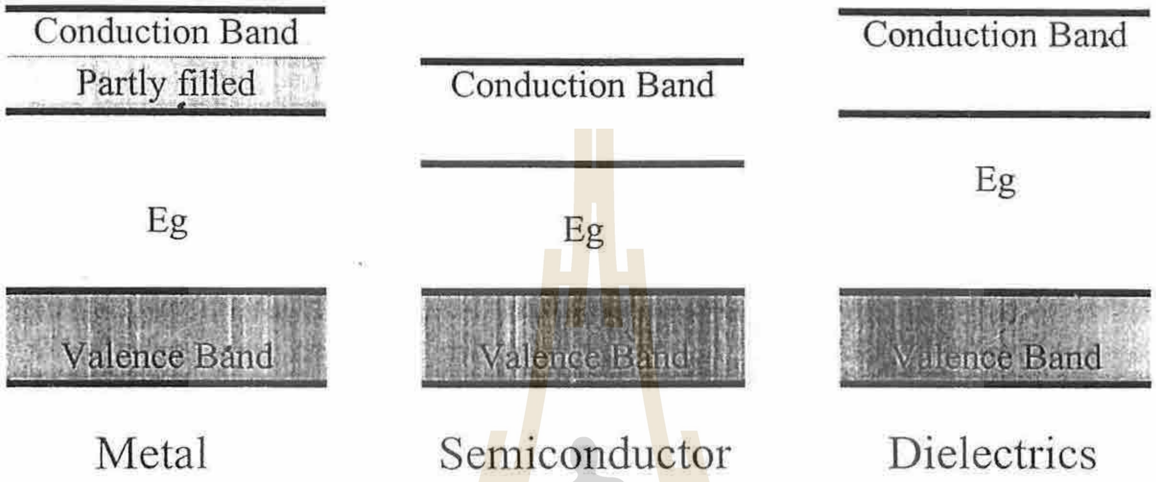
For Example: He- d line :5875.6Å

- 5875.6Å : Wavelength (Classical)
- 587.56nm : Wavelength
- 0.58756μm : Wavelength(quite few)
- 2.11eV : Photon Energy
- 16,969cm^{-1} : Wavenumber

2. Absorption and Reflection

The differential equation which describes the rate of change of the intensity, I, due to the absorption of light in a material in the positive x direction is given by $dI/dx=-\beta Io$. Where β is the absorption, ε is

Energy Band(Band Structure)



Band Gap: Eg

Eg < 3eV
(>413nm)

Eg > 3eV
(<413nm)

$\lambda = 1239.8/eV(nm)$

Materials	Eg(eV)	Materials	Eg(eV)
Diamond	5.4*	CdSe	1.74
Si	1.14	TiO_2*	3.03
Ge	0.67	MgO	≈6.8
CdS	2.42	SiO_2	≈10.0

At 300°K, *:0°K

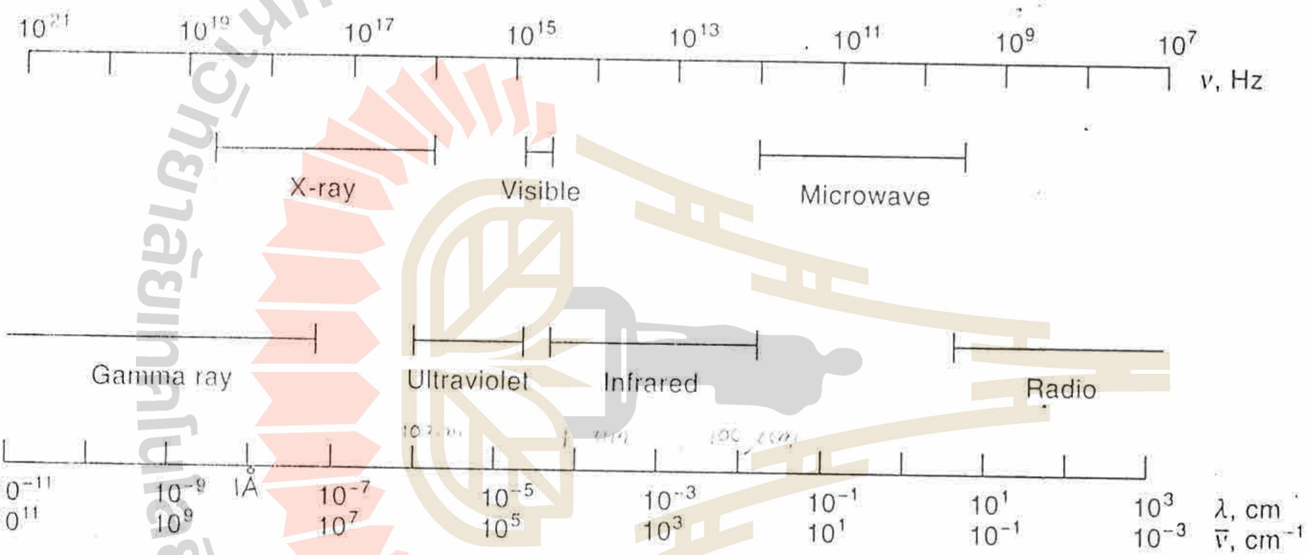


FIGURE 5–1 Regions of the electromagnetic spectrum.

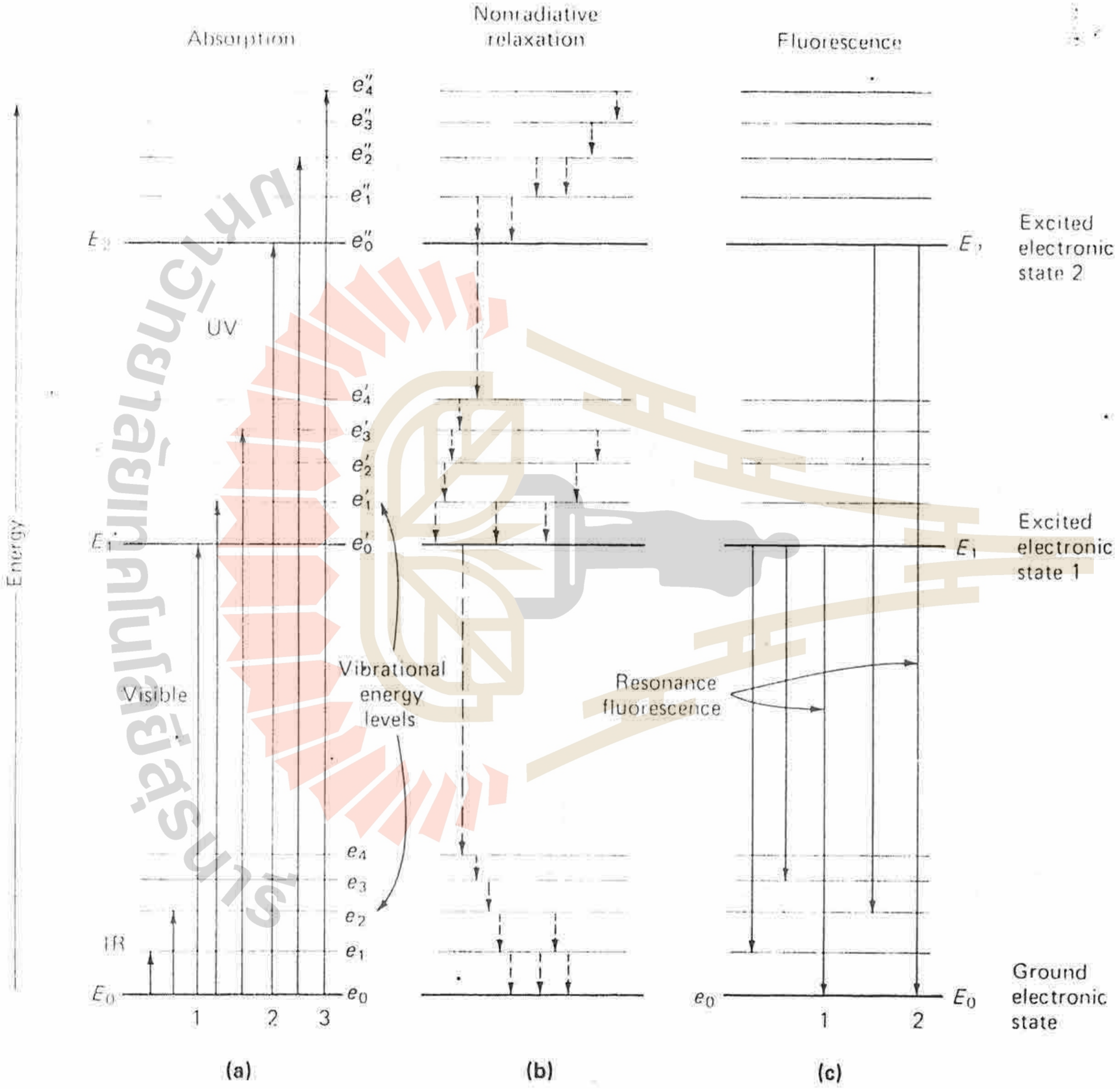


FIGURE 5–16 Partial energy-level diagram for a fluorescent organic molecule.

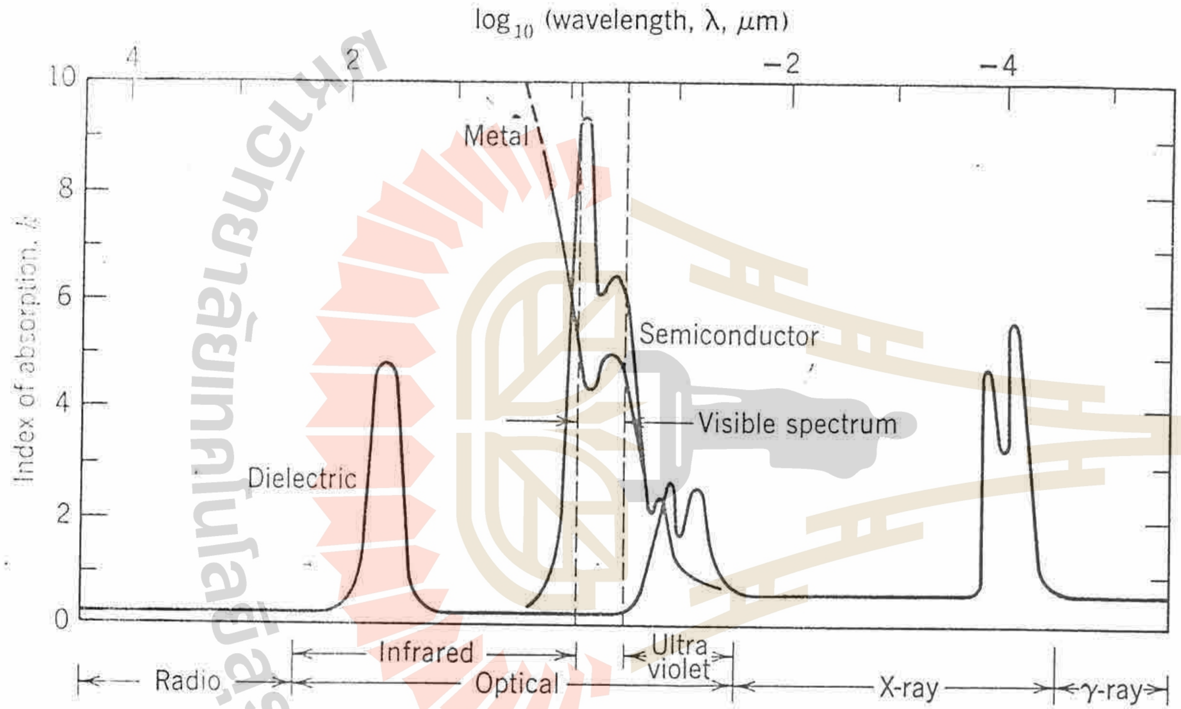
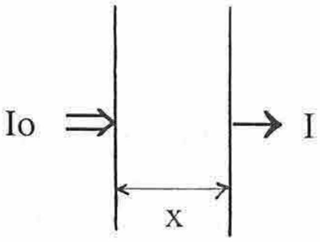


Fig. 13.1. Frequency variation of the index of absorption for metals, semiconductors, and dielectrics.

extinction coefficient(liter/mole·cm) and c is the concentration (mole/liter).



$$dI / I_O = -\beta dx$$
$$I / I_O = \exp(-\beta x)$$
$$\beta = \varepsilon c$$

Therefore, the transmittance is given by

$$T = I / I_O = \exp(-\beta x) = \exp(-\varepsilon c x)$$
$$\beta x = \varepsilon c x = \mathrm{Ln}(I_O / I)$$

Overall transmittance T' is given by ($\theta = 0$, normal incidence)

$$T' = I / I_O = (1-R)^2 \exp(-\beta x)$$

where

$$R = [(n-1)^2 + k^2] / [(n+1)^2 + k^2]$$

where n is the refractive index, k the coefficient of absorption. If one can assume $n >> k$, above equation is simplified to be

$$R = (n-1)^2 / (n+1)^2$$

And, if k is much larger than n($k >> n$), R becomes and appreciable fraction of unity. Spectrometers may record absorption as percent transmission $[(I/I_O) \times 100]$ or as optical density(O.D.) which is defined

$$\mathrm{O.D.} = \mathrm{Log}_{10}(I_O / I) = (1/2.303)\mathrm{Ln}(I_O / I)$$

Finally, the use of the decibel(dB) as a unit of optical loss is more common today because the influence of wave guide technology.

$$10\mathrm{dB} = 1 \cdot \mathrm{O.D.}$$

3. Transparency

How can the transparency(in visible region) of materials be accomplished? They are no intrinsic absorption and no scattering.

The coefficient of scattering of light by small particles in transparent matrix can be given by

$$\sigma' = 24\pi^3 Fv / \lambda^4 \cdot [(n^2 - n_o^2)/((n^2 + n_o^2)]^2 n_o^4 V$$

where λ is the wavelength, Fv is the volume fraction of particles, n is the refractive index of particles, n_O is the refractive index of matrix, and V is the volume of particles ($4\pi R^3/4$). In this equation, the following conditions would be required for transparency of materials:

- The smaller the refractive index difference between particles and matrix.
- The smaller sizes of particles than the wavelength.
- The smaller birefringence of crystal particles

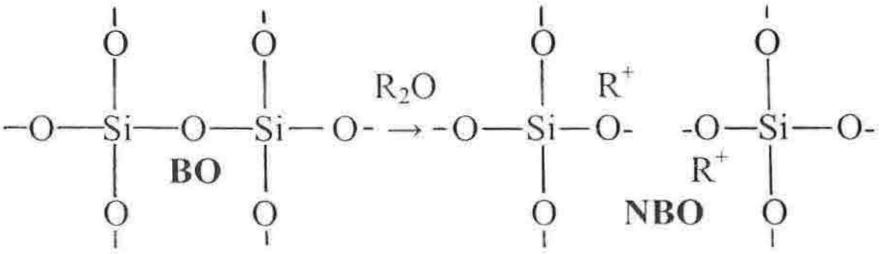
4. UV Absorption

The availability of higher purity glasses during the past few years has stimulated work on the UV absorption of glasses. Strong impurity cation absorption, especially that associated with transition metals such as Fe, Cr, and Cu, tends to dominate the near-UV absorption of most commercial glasses, obscuring the intrinsic tail of the fundamental absorption edge. Thus, high-purity materials are absolutely necessary for the UV spectroscopy.

Stevels was the first to suggest that the intrinsic absorption edge of an oxide glass correspond to the transition of a valence electron of an oxygen ion in the glass network to an excited state. It was assumed that electrons which participate in strong chemical bonds would require the higher energy(or shorter wavelength) for excitation. For the simple glass forming oxides, Stevels predicted an edge shift to shorter wavelength in the order B_2O_3, SiO_2 and P_2O_5, which corresponds to the experimental values of

B_2O_3 : 170nm
SiO_2 : 160nm
P_2O_5 : 145nm

If, however, the glass forming network is disrupted by the introduction of network modifying alkali or alkaline earth ions which produce singly bonded oxygen ions (non-bridging oxygen ion, NBO),



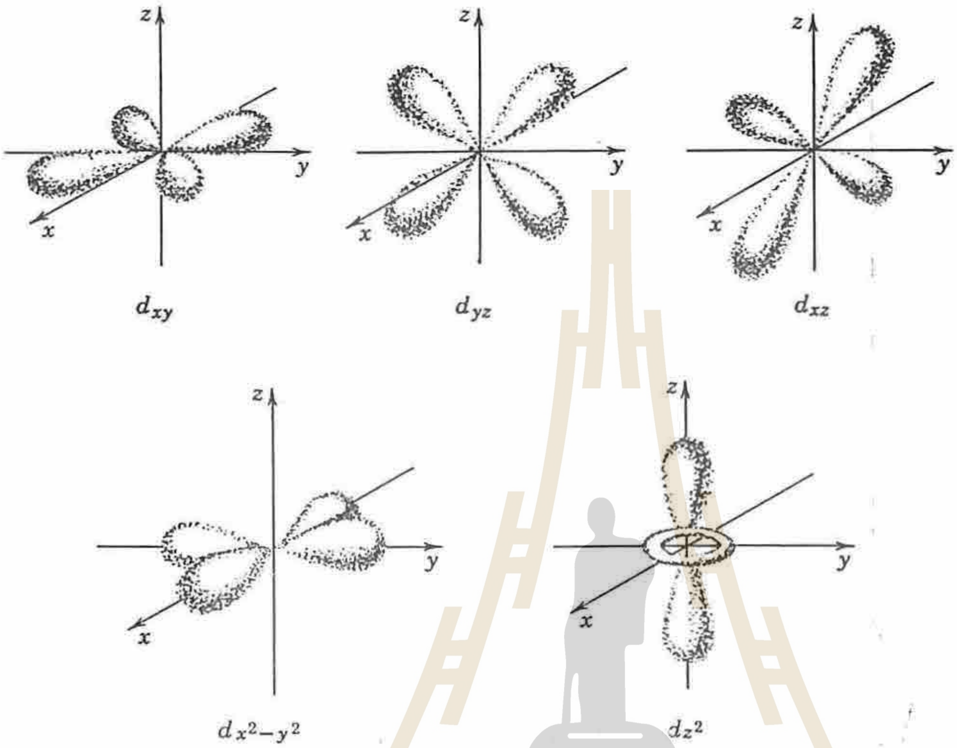


Fig. 13.20. The five *d* orbitals.

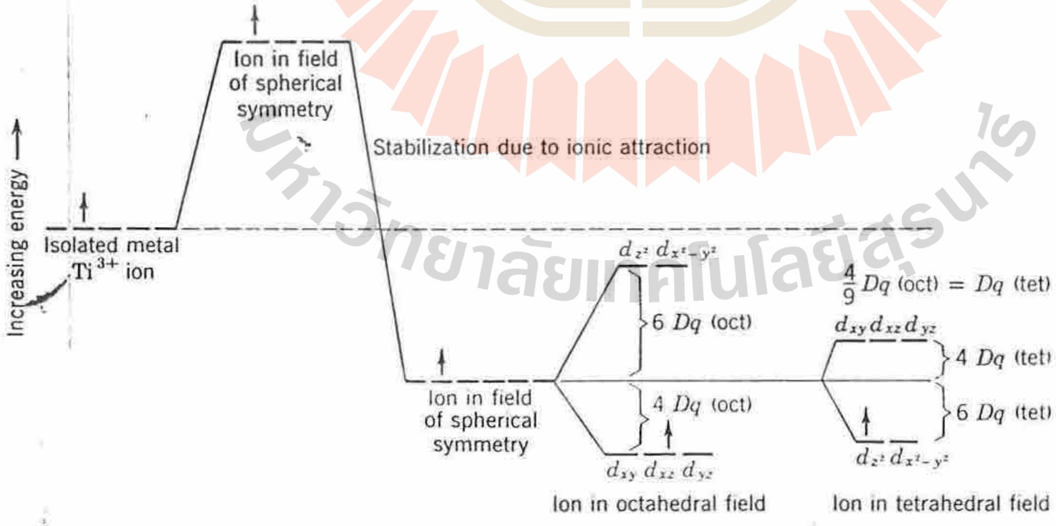


Fig. 13.21. Crystal field energy relationships for Ti^{3+} ion in an octahedral and tetrahedral field.

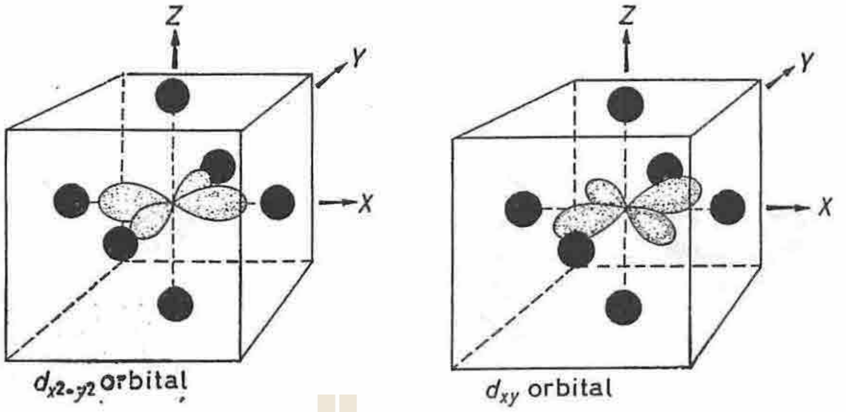


Figure 3. The $d_{x^2-y^2}$ *and* d_{xy} *orbitals in an octahedral ligand field*

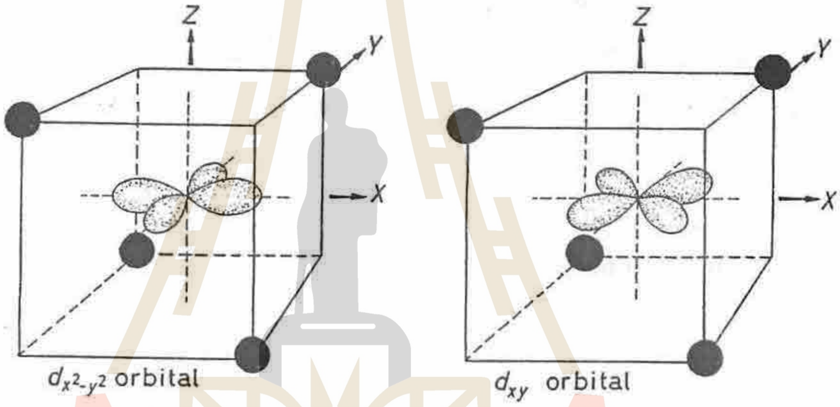


Figure 4. The $d_{x^2-y^2}$ *and* d_{xy} *orbitals in a tetrahedral ligand field*

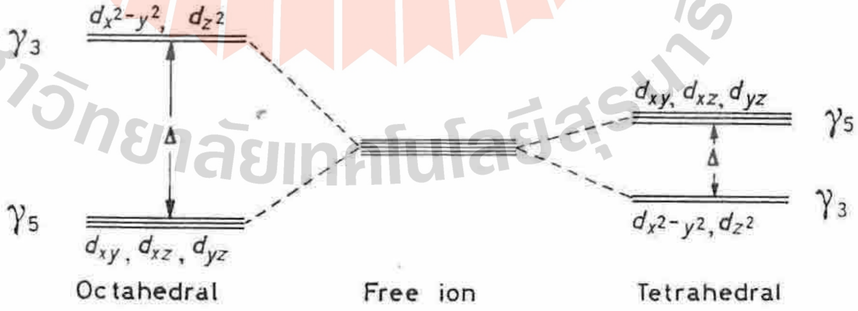


Figure 5. Energy levels of the d*-orbitals in octahedral and tetrahedral fields*

TABLE I

TRANSITION METAL IONS IN GLASSES

Configuration	Ion	Color
d^0	Ti^{4+}	Colorless
	V^{5+}	Faint yellow to colorless
	Cr^{6+}	Faint yellow to colorless
d^1	Ti^{3+}	Violet-purple
	V^{4+}	Blue
	Mn^{6+}	Colorless
d^2	V^{3+}	Yellow-green
d^3	Cr^{3+}	Green
d^4	Cr^{2+}	Faint blue
	Mn^{3+}	Purple
d^5	Mn^{2+}	Light yellow
	Fe^{3+}	Faint yellow
d^6	Fe^{2+}	Blue-green
	Co^{3+}	Faint yellow
d^7	Co^{2+}	Blue-pink
d^8	Ni^{2+}	Brown-purple
d^9	Cu^{2+}	Blue-green
d^{10}	Cu^{+}	Colorless

TABLE II

RARE EARTH IONS IN GLASSES

Configuration	Ion	Color
$4f^0$	La^{3+}	None
	Ce^{4+}	Weak yellow
$4f^1$	Ce^{3+}	Weak yellow
$4f^2$	Pr^{3+}	Green
$4f^4$	Nd^{3+}	Violet-pink
$4f^4$	Pm^{3+}	None
$4f^5$	Sm^{3+}	None
$4f^6$	Sm^{2+}	Green
	Eu^{3+}	None
$4f^7$	Eu^{2+}	Brown
	Gd^{3+}	None
$4f^8$	Tb^{3+}	None
$4f^9$	Dy^{3+}	None
$4f^{10}$	Dy^{2+}	Brown
	Ho^{3+}	Yellow
$4f^{11}$	Er^{3+}	Weak pink
$4f^{12}$	Tm^{3+}	None
$4f^{13}$	Tm^{2+}	None
	Yb^{3+}	None
$4f^{14}$	Lu^{3+}	None

Table 13.6. Crystal-Field Data for Transition Metal Ions

		Hydrates		Oxide
Number of d electrons	Ion	Octahedron 10 Dq/cm^{-1}	Tetrahedron 10 Dq/cm^{-1}	Octahedron 10 Dq/cm^{-1}
1	Ti^{3+}	20,300	9000	6000
2	V^{3+}	18,000	8400	
3	V^{2+}	11,800	5200	
	Cr^{3+}	17,600	7800	16,800
4	Cr^{2+}	14,000	6200	
	Mn^{3+}	21,000	9300	
5	Mn^{2+}	7500	3300	7300–9800
	Fe^{3+}	14,000	6200	12,200
6	Fe^{2+}	10,000	4400	9520
	Co^{3+}	18,100	7800	
7	Co^{2+}	10,000	4400	
8	Ni^{2+}	8600	3800	8600
9	Cu^{2+}	13,000	5800	
10	Zn^{2+}	0	0	

1 eV = 8066 cm^{-1} = 23.06 kcal/mole.

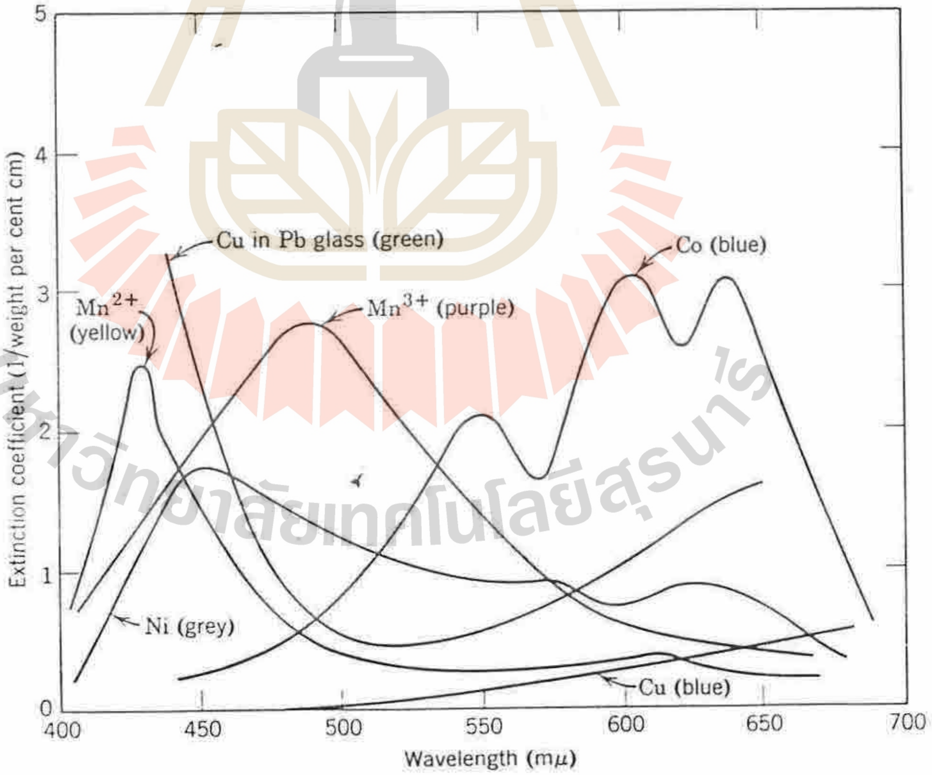


Fig. 13.22. Extinction coefficients for several ions in glasses.

the K_2O glasses contain the highest proportion of Co^{2+} in this coordination and the Li_2O glasses the least.

All the alkali silicate glasses containing CoO have similar absorption spectra to high alkali borates. They are deep blue in color and presumably contain only Co^{2+} in four fold coordination. This has been attributed to the fact that the initial addition of alkali to a silicate melt produces non-bridging oxygen ions whereas this does not happen in the borate system. The availability of non-bridging oxygens has been regarded as favoring the increase in the coordination number of Co^{2+} ion.

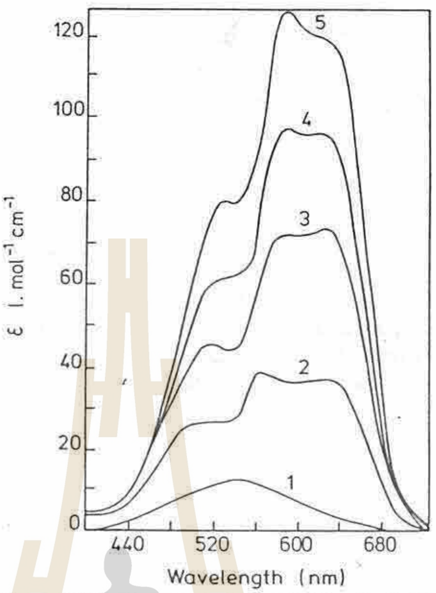


Fig. 113- The absorption spectra of Na_2O-B_2O_3 glasses containing Co^{2+}. Na_2O contents in mol%: 1, 13%; 2, 22.5%; 3, 26.5%; 4, 30.2%; 5, 33.0%.

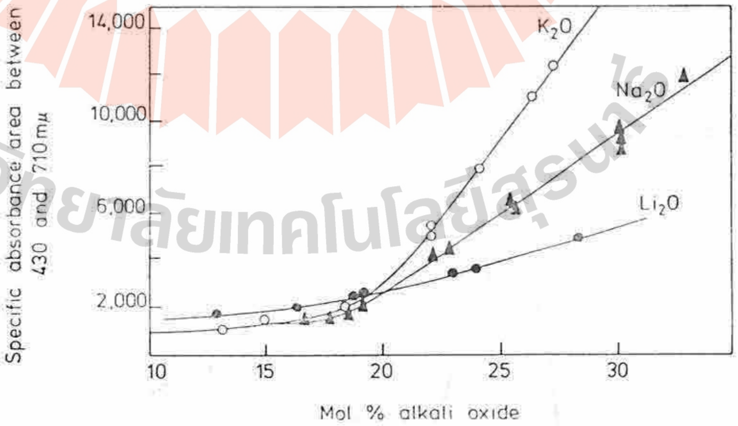


Fig. 114. The effect of alkali content in alkali borate glasses on the strength of the absorption due to Co^{2+} in tetrahedral co-ordination. (Paul and Douglas, 1968).

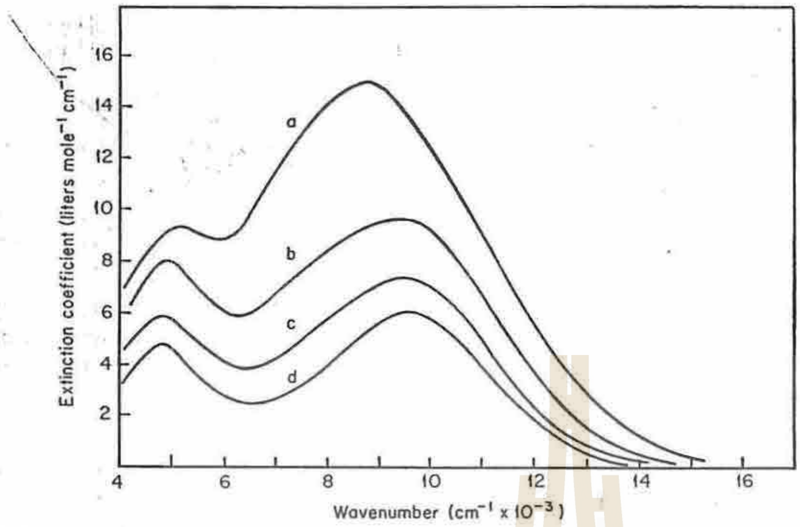


Fig. 27. Absorption spectra associated with Fe^{2+} in tetrahedral (2.1-μm band) and octahedral (1.05-μm band) symmetry in binary alkaline earth phosphate glasses. (a) $MgO \cdot P_2O_5$, (b) $CaO \cdot P_2O_5$, (c) $SrO \cdot P_2O_5$, and (d) $BaO \cdot P_2O_5$. (After Edwards *et al.*, 1972.)

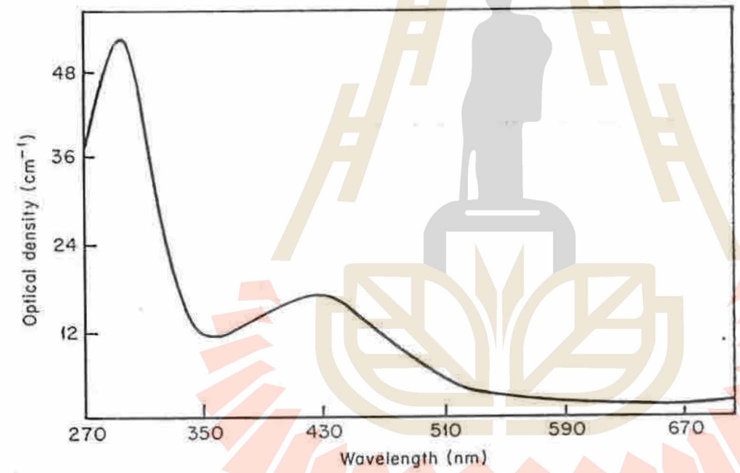


Fig. 28. Principal absorption bands in carbon amber glasses lie near 0.295 and 0.425 μm and have been associated with Fe^{3+} in tetrahedral coordination with one oxygen replaced by a sulfur. ($3K_2O \cdot 7SiO_2$ glass, 0.051 wt % iron, 0.125 wt % sulfur). (After Douglas and Zaman, 1969.)

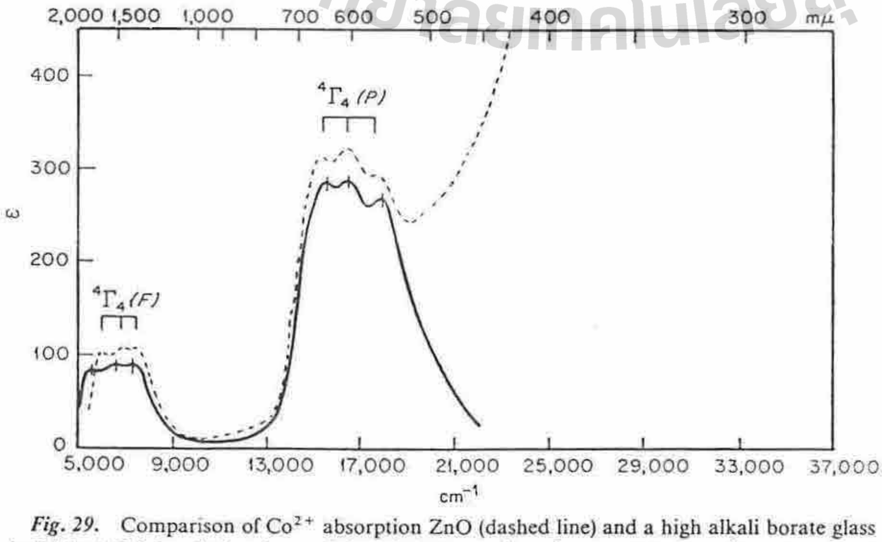


Fig. 29. Comparison of Co^{2+} absorption ZnO (dashed line) and a high alkali borate glass (solid line). Triply split bands near 0.6 μm (16,500 cm^{-1}) and 1.5 μm (7000 cm^{-1}) are associated with Co^{2+} in tetrahedral coordination. (After Bates, 1962.)

ions. The mathematical details of the ligand field theory of glasses are available in the references and will not be derived here, but a few elementary concepts are useful for discussing the absorption of colored glasses. The colors of each transition metal ions can be seen in the references.

①. Ligand Filed Theory

In a field free environment (a free ion) the five d orbitals are degenerate: they have same energy. In the presence of a crystal field (ligand field), however, as in a single crystal, all the d orbitals no longer have the same energy but are split into groups. This can be illustrated by the simple case of Ti^{3+} ion, which has only one d electron, surrounded by six negative ions arranged at the corners of an octahedron. In the presence of such a field, the electronic energy in the two orbitals which lie along the axes, dz^2 and $dx^2\text{-}y^2$, are raised relative to the free ion because of repulsion from surrounding anions. In contrast, the electronic energy of other three orbitals, which do not lie along the axes, is raised by a small amount. This splitting of the d levels thus reflects the tendency of the electron to avoid regions in which the field of the ligands is largest.

If the Ti^{3+} ion is surrounded by four negative ions arranged at the corners of a tetrahedron, the electronic energy in the dz^2 and $dx^2\text{-}y^2$ is less than that in the dxy, dyz, dxz orbitals, and the magnitude of the splitting in this case is smaller than in the octahedral field.

The total energy difference between the higher and lower energy levels is denoted 10 Dq.

$$\underline{\mathbf{4\ /\ 9\ Dq(\ Oct.\ )\ =\ Dq\ (\ Tetr.\ )}}$$

②. Effect of Glass Composition

It is worth looking briefly at the effects of changes of glass composition on the absorption spectra of Co^{2+} and Ni^{2+} ions. Because these ions in almost all silicate, borate, and phosphate compositions melted under normal conditions only the divalent ions are present.

As the glass composition is made more basic by increasing the alkali content, the color of borate and silicate glasses changes from pink to an intense blue. This is due to a change in the oxygen coordination number of the cobalt ion from 6(octahedral symmetry) to 4(tetrahedral symmetry). This effect is shown in below figure. And also below figure shows how the area under the absorption curve between the wavelengths 430 and 710nm increases with increasing R_2O content for three alkali borate systems. It is suggested that the inflection at 20mole % R_2O indicates that the change to tetrahedral coordination of the Co^{2+} ion begins at this composition. The curve also indicates that, above inflection, 260-290nm(4.7-4.3eV). And also a range of PbO-SiO_2 glasses containing 24.6-65 mole % PbO and a cutoff shift with increasing PbO concentration from 340nm to 400nm, the high lead glasses exhibiting the well known yellow colour from the tail of the Pb^{2+} band.

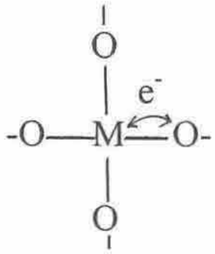
Phosphate glasses also tend to exhibit excellent UV transmission.

5. Absorption in Visible Region

The color generation in visible region is caused by impurities. They are;

① Transition Metal Ions

- Near UV : Charge transfer absorption(strong absorption)



≈200nm ~ Visible
strong absorption

- Visible Region : Ligand field coloration(Ligand Field Theory)

② Rare Earth Ions

- Mechanism is almost same as transition metal ions.
- Optical absorption associated with the rare earth ions consists of many very weak, sharp lines ranging from near UV to near IR.

③ Metallic particles and others

- Mie's theory(Electro-magnetic wave theory)
- Surface plasmon resonance absorption(Metallic particles)
- Band Gap Absorption (Semiconductor Particles)

(1). Transition Metal Ions and Rare Earth Ions

The most important classes of impurities found in oxide glasses are the transition metal elements(Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) which introduce optical absorption bands associated with excitation of 3d electrons in partially filled inner shells. When these ions are introduced into the glass network, energy levels of the free ions are split and shifted by the electrostatic fields of the nearest-neighbor anions, typically oxygens. Since the field of a metal ion falls off extremely rapidly with distance, only interactions with adjacent atoms, molecules, and ions (termed ligands) need to be considered. Ligand field theory or crystal field theory was developed to calculate the splittings and transitions which will arise for a given electronic configuration in a specified symmetry. In glasses, ligand field theory has been used with good success to identify most of the absorption bands associated with transition metal

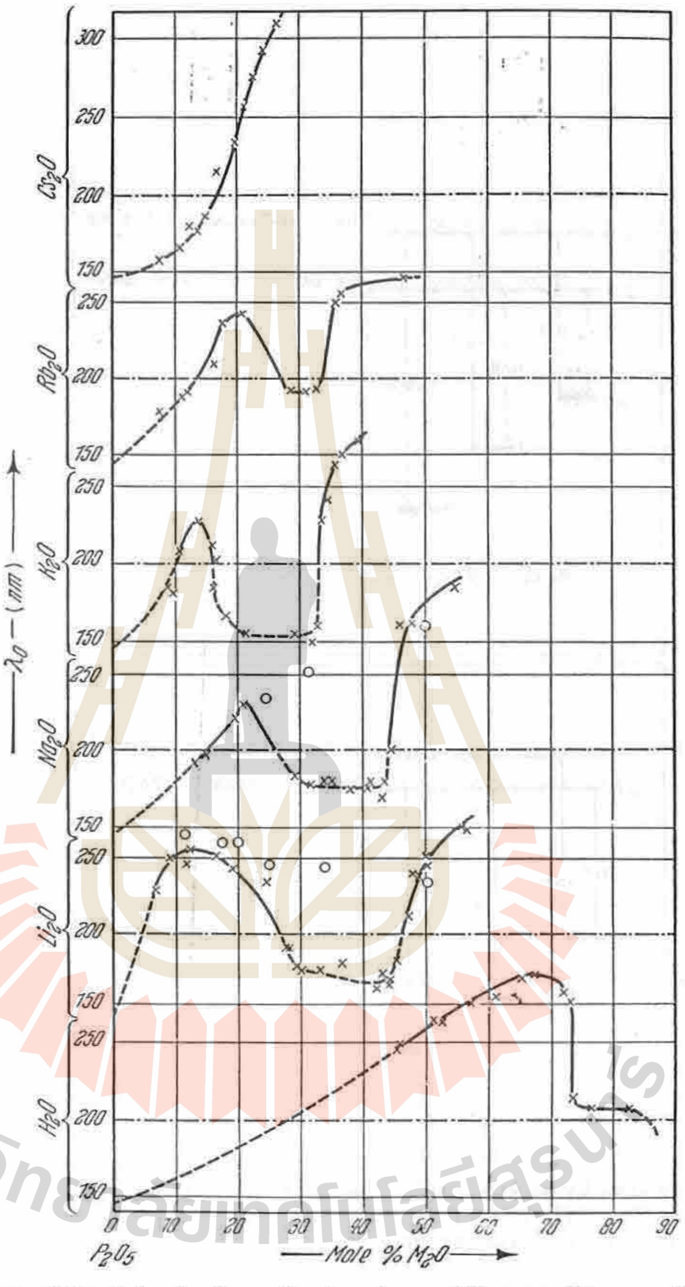


Fig. 19. Effects of the introduction of network modifiers on the uv cutoff of phosphate glasses. (After Kordes and Nieder, 1968.)

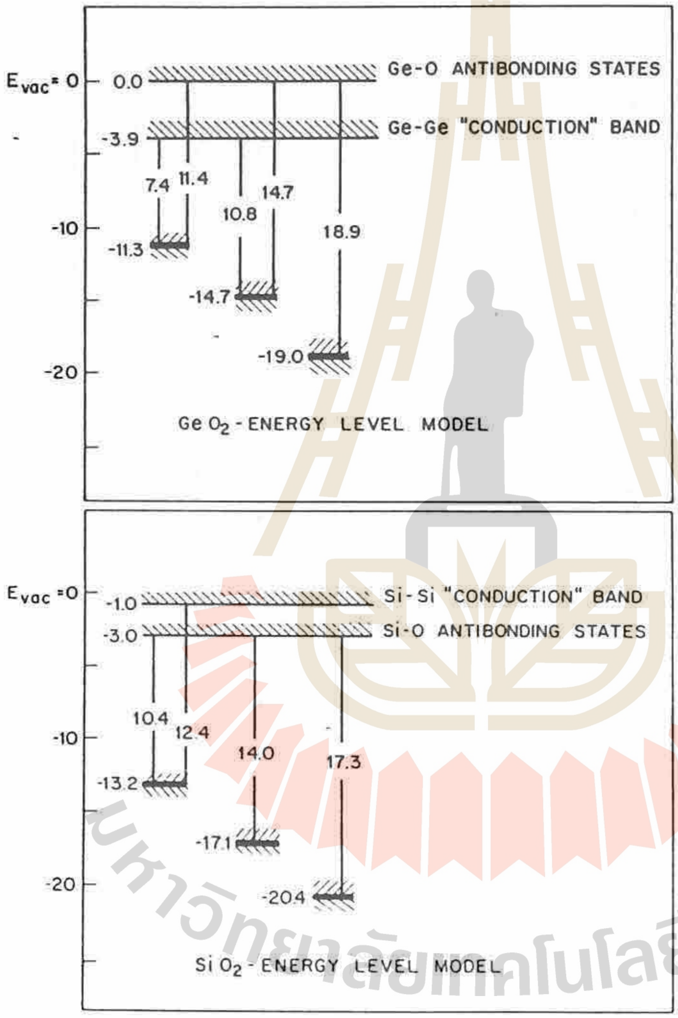


Fig. 3. Energy level models for SiO_2 and GeO_2 consistent with experimental data, including the optical reflectance data of Fig. 2. Transitions from various valence state levels to antibonding and conduction band states are shown. (After Rowe, 1974.)

$L_2O - SiO_2$: 6.6 eV = 188 nm
$Na_2O - SiO_2$: 5.97eV = 208 nm
$K_2O - SiO_2$: 5.80eV = 214 nm

The edge increased to longer wavelength by the addition of MgO, CaO, SrO, BaO. B_2O_3 addition was observed to shift the edge to shorter

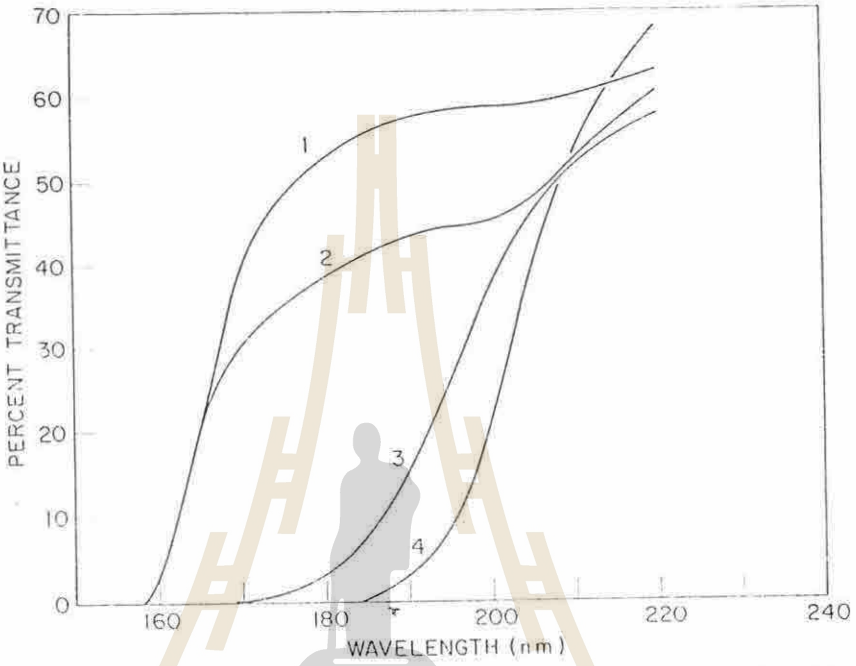
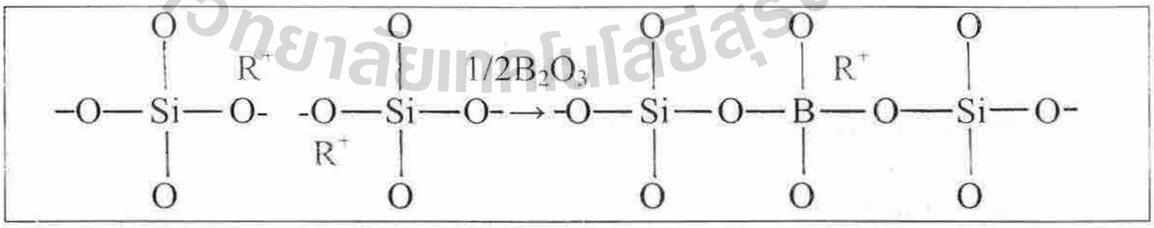


Fig. 4. The effect of aluminum on the uv absorption of alkali-doped silica. Edge shifts to shorter wavelengths upon introduction of aluminum. Sample thickness is 1 mm. Fused silica (1) 0.5 mole % Na + 0.5 mole % Al; (2) 0.2 mole % K + 0.2 mole % Al; (3) 0.5 mole % Na; (4) 0.2 mole % K. (After Sigel, 1971.)

wavelength, apparently because of the reduction of the NBO concentration in the glass by the formation of four coordinated boron.



$$-\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}-\text{O}^{-}\;\overset{\text{R}^{+}}{}\;\underset{\text{R}^{+}}{}\;{}^{-}\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}-\text{O}- \xrightarrow{1/2\text{B}_2\text{O}_3} -\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}-\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{B}}}\overset{\text{R}^{+}}{}-\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}-\text{O}-$$

Glasses containing PbO absorb very strongly in the UV. $Na_2O \cdot 3SiO_2 \cdot 2PbO$ glass was characterized by a structureless edge with $\alpha = 1 cm^{-1}$ at $\lambda = 350 nm$(3.55eV). For lead silicate glasses containing 50-70 mole % PbO, a triplet reflection peak attributed to Pb^{2+} was observed between

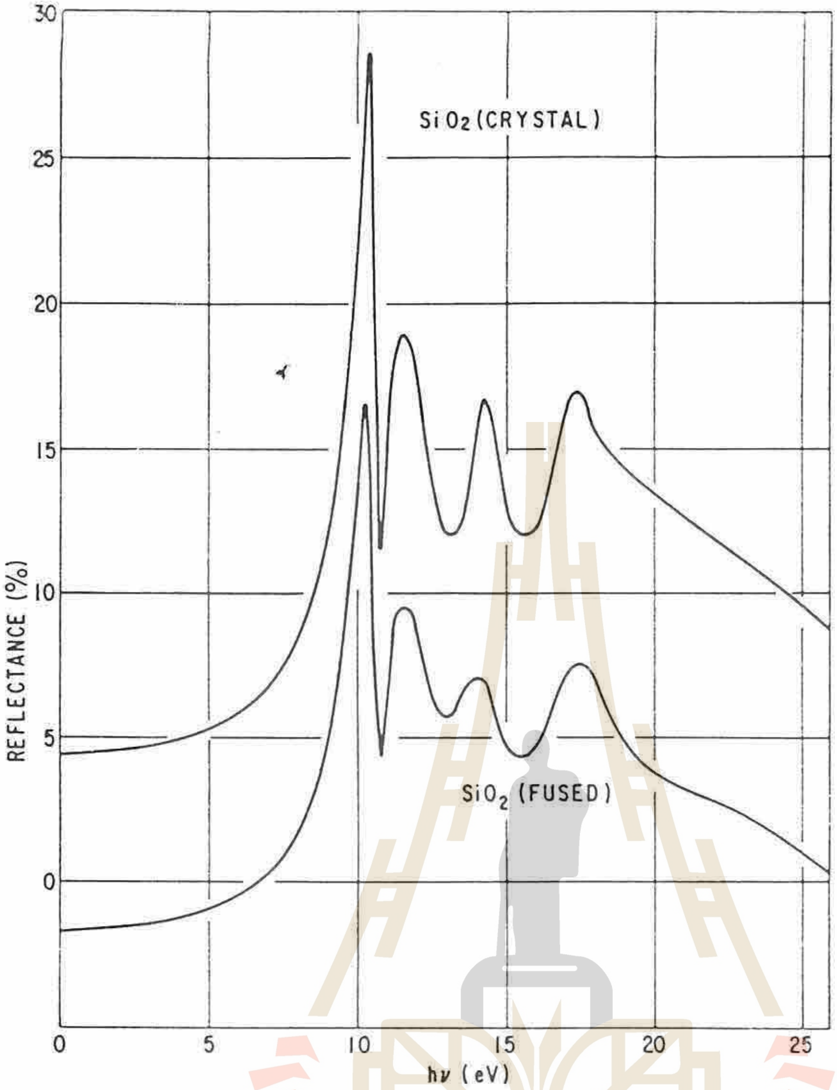


Fig. 2. The reflectance spectra of α-quartz and fused silica. The values of fused silicia have been lowered by 5%. (After Philipp, 1966.)

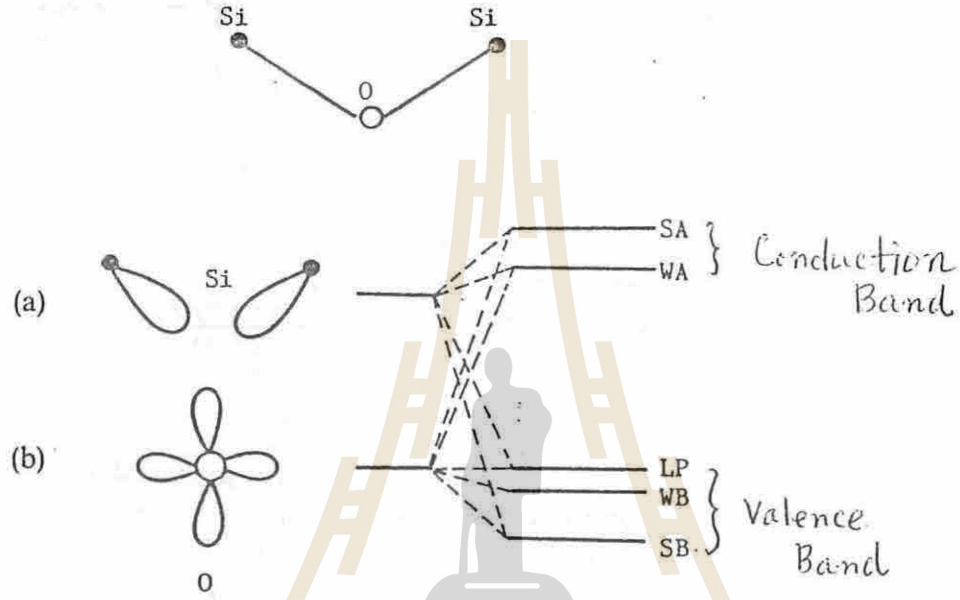
the average chemical bond strength of the network will be reduced and electron excitation will require less energy. The general weakening of the bonding should manifest itself as a shift of the UV edge to longer wavelength.

The ultraviolet absorption of silicate glasses arises from three principle sources:

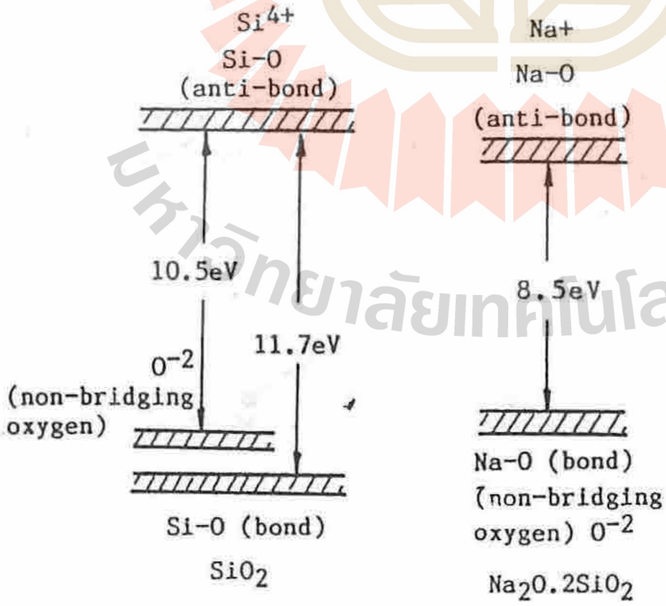
(1). Absorption intrinsic to electronic excitations of the Si – O network.
(2). Absorption arising from the introduction of network modifying and/or network forming cations.
(3). Absorption resulting from the presence of impurities, particularly charge transfer spectra of transition metal ions.

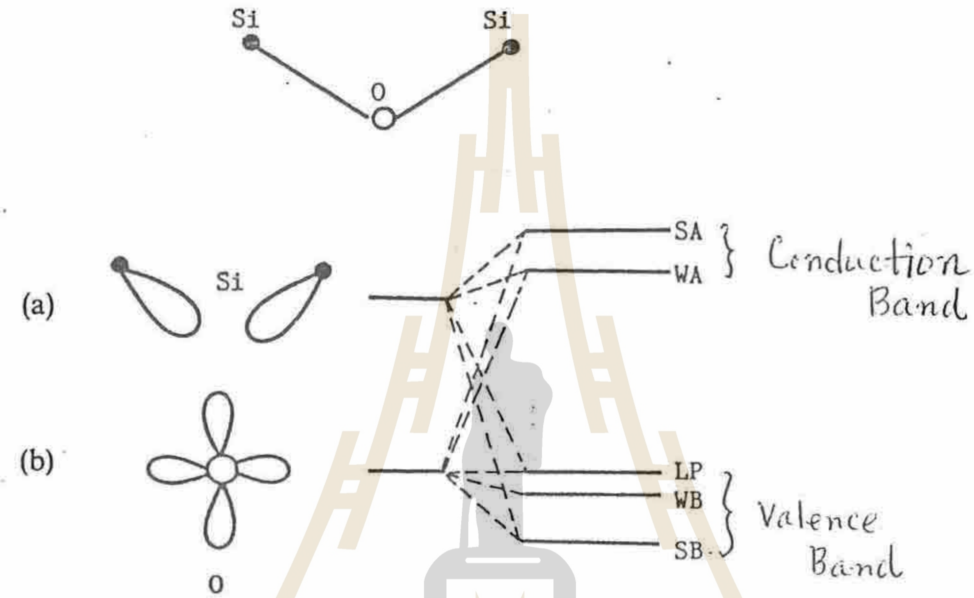
(1). Compositional Effect

In alkali-silicate glasses, the UV absorption edges are obtained experimentally:

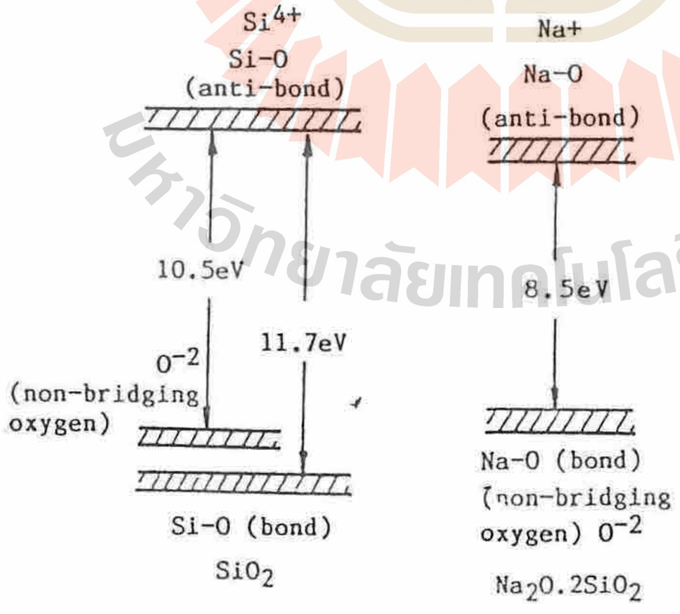


Electronic transition of silica glass. **a** Hybrid state sp^3 of silicon atom; **b** p state of oxygen atom





Electronic transition of silica glass. **a** Hybrid state sp^3 of silicon atom; **b** p state of oxygen atom



Change in glass composition have a similar effect on the symmetry of Ni^{2+} ions and hence on the color of the glass. Increasing the alkali content results in a change from octahedral to tetrahedral symmetry, although it has been suggested that there may be an intermediate region in which the Ni^{2+} ions are surrounded by four oxygen ions at the corner of square.

The general effect of making the glass composition more basic, i.e. of increasing the R_2O content in binary borate, silicate and phosphate systems is to increase the proportion of the transition element in the higher valence state. The melt becomes more oxidizing. At a given molecular percentage of R_2O, the K_2O melt is most oxidizing and the Li_2O melt the least.

③. Redox equilibria of Transition Metal Ions in Glass

Most of the transition metal are multivalent, and when an oxide of one of these metals is dissolved in glass an equilibrium between two types of ion representing different valence state of the metal.

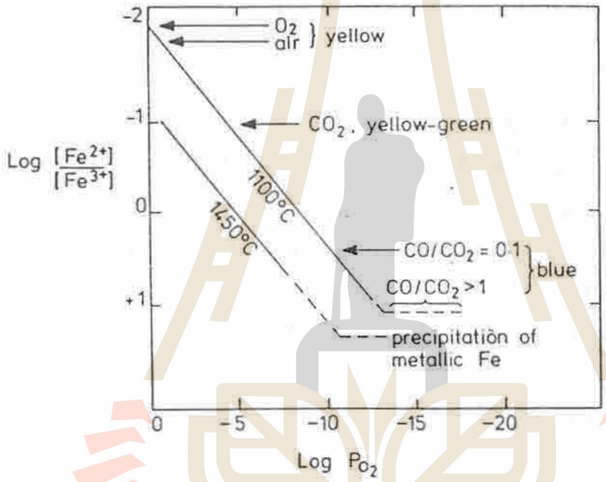


Fig. 115. The effect of the partial pressure of oxygen on the $[Fe^{2+}]/[Fe^{3+}]$ ratio in a Na_2O-$2SiO_2$ glass (Johnston, 1964).

$$M^{n+} \leftrightarrow M^{m+} + (m/n)O_2$$

The color of the glass depends on the relative proportions of these ions. The equilibrium ratio is affected by a number of factors: the partial pressure of oxygen in the atmosphere of the furnace in which the glass has been melted, the melting temperature, the composition of the glass and the presence of other multivalent ions in the glass. An equilibrium ratio is established only if the melting temperature is high enough and the melting time is sufficiently long. Even at melting temperature of the order

Since the concentrations of the iron ions in the glass are low, it is reasonable to assume that their activities are proportional to their concentrations. One can also assume that the oxygen ion activity in a given glass and at a given temperature is constant and is not significantly affected by any change in the balance of the reaction. One would therefore expect the following equation to hold

$$\mathrm{Log}((Fe^{2+})/(Fe^{3+})) = \mathrm{Log}([Fe^{2+}]/[Fe^{3+}]) = \mathrm{Log}(P_{O2}/4)$$

here (Fe^{2+}) and (Fe^{3+}) are the concentration of the respective ions in the glass. The above result (figure) fit this equation very well.

Increasing the melting temperature increases the proportion of Fe^{2+}. Thus for the glass which has been brought into equilibrium with air (P_{O2}) at 1100°C only 1.5% of the iron of Fe^{2+}. At 1450°C this increases to 9%. Because the iron is predominantly ferric, the color of both glasses at room temperature is yellow. By melting in furnace atmosphere which are mixtures of CO and CO_2, very low oxygen partial pressures are readily obtained and the oxygen partial pressure can be calculated from the composition of the gas mixture. The results show the expected increase in the (Fe^{2+})/(Fe^{3+}) ratio as the CO/CO_2 ratio is increased. The glasses containing high percentage of Fe^{2+} ions are blue in color.

A number of similar studies have been made of the redox equilibria of other transition elements, Tl^{3+}/Ti^{4+}, Ce^{3+}/Ce^{4+}, Mn^{2+}/Mn^{3+}, Sb^{3+}/Sb^{5+} and Sn^{3+}/Sn^{4+}, and Cu^{+}/Cu^{2+}. In all systems, increasing the melting temperature and decreasing the oxygen partial pressure in the atmosphere has the same effect of moving the balance of the equilibrium towards the lower valence state.

Similar but even greater problems arise when one is dealing with a situation in which the glass contains more than one mutivalent element. One has to contend with such situations in practice. Some commercial colored glasses do contain more than one multivalent transition metal.

A number of studies have been made of the equilibrium between pairs of redox oxides in glass melts. And the results have been discussed in terms of the thermodynamics of the postulated reactions. The commonly used starting point for these discussions is an "***Ellingham diagram***"
which shows the variation with temperature of the change in free energy when oxide reacts with one mole of oxygen to form a second oxide in which the metal has a higher valency.
It is important to remember that this and similar diagrams refer to the pure oxides and not to these oxides when dissolved in a glass.

To illustrate the use of an Ellingham diagram, consider the following reactions:

$$(1)\quad As_2O_3 + O_2 \leftrightarrow As_2O_5$$
$$(2)\quad 4FeO + O_2 \leftrightarrow 2Fe_2O_3$$

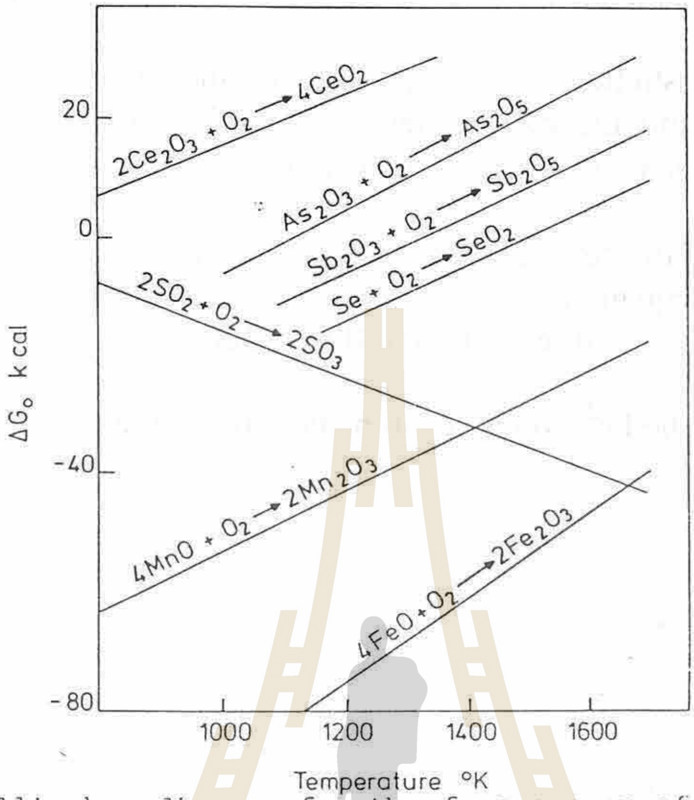


Fig. 117. Ellingham diagram for the free energy of reaction per mole of oxygen of some redox systems of interest in glass making.

At 1600°K the free energy changes for these reactions are respectively ΔG_1=+20Kcal and ΔG_2=-50Kcal. If one can consider the reaction

$$4FeO + As_2O_5 \leftrightarrow 2Fe_2O_3 + As_2O_3$$

the free energy change will be $\Delta G = \Delta G_1 - \Delta G_2$=-70Kcal. Consequently the reaction will go to the right and As_2O_5 will oxidize FeO to Fe_2O_3. Similarly one can show that any redox pair lying near the top of the diagram will oxidize those lying below it.

When these oxides are dissolved in glass it is not to be expected that the behavior will be exactly as predicted by the Ellingham diagram. However it is found that for the reactions the equilibrium is predominantly to the right as predicted, unless there is insufficient cerium or arsenic oxide present for complete oxidation of the iron to be possible.

$$Ce^{4+} + Fe^{2+} \leftrightarrow Fe^{3+} + Ce^{3+}$$
$$Cr^{6+} + 3Fe^{2+} \leftrightarrow 3Fe^{3+} + Cr^{3+}$$
$$As^{5+} + 2Fe^{2+} \leftrightarrow 2Fe^{3+} + As^{3+}$$

of 1400°C it may take many hours for equilibrium to be reached in a silicate glasses. When melting such glasses continuously on a tonnage scale in a large tank furnace it is doubtful if equilibrium with the furnace atmosphere is established in more than a small fraction of the glass melted.

A number of studies have been made of the effect of the oxygen partial pressure and the melting temperature. Below figure shows the equilibrium between Fe^{2+} and Fe^{3+} ions in a $Na_2O{\cdot}2SiO_2$ glass containing 2wt% of Fe_2O_3.

The equilibrium between the ions and the atmosphere may be expressed by the equation

$$4Fe^{2+} + O_2 \leftrightarrow 4Fe^{3+} + 2O^{2-}$$

The oxidation of the Fe^{2+} ion is accompanied by the transfer of oxygen to the glass from the atmosphere, the oxygen atoms acquiring electrons from the Fe^{2+} ions, thus changing into oxygen anions which are incorporated into glass structure. Once equilibrium has been attained, the glass is rapidly cooled to room temperature. The equilibrium constant K of the Fe^{2+}/Fe^{3+} reaction is given by

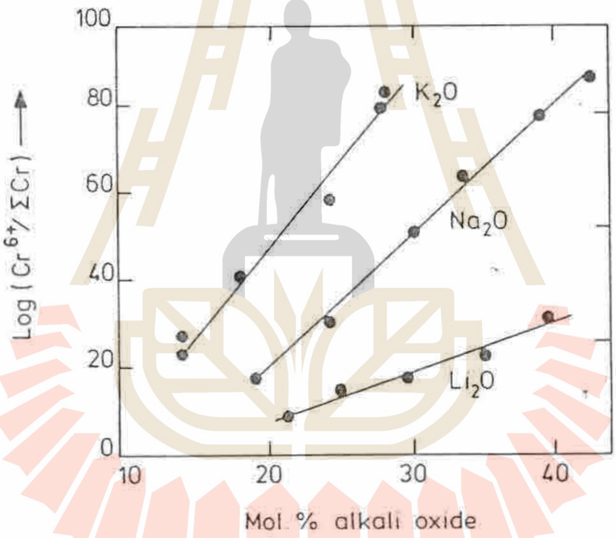


Fig. 116. The effect of glass composition on the ratio $(Cr^{6+})/(Cr^{6+} + Cr^{3+})$ in alkali silicate glasses. (Nath and Douglas, 1965).

$$K = ([Fe^{3+}]^4 \cdot [O^{2-}]^2)/([Fe^{2+}]^4 \cdot P_{O2})$$

where $[Fe^{3+}]$, $[Fe^{2+}]$ and $[O^{2-}]$ represent the activities of these ions in the glass melt and P_{O2} is the partial pressure of oxygen in the atmosphere.

(2). Metallic Particles and Semiconductor Particles

The brilliant reds and yellows of certain Au, Ag and Cu-doped glasses has been well-known since the middle of the 17th century. Some metals and semi-conductors are slightly soluble in oxide glasses. By suitable heat treatment at temperatures below the melting point they can be made to precipitate out from solution to give a large number of particles of colloidal size. The glass is colored, the color depending on the optical properties of the precipitated metal or semi-conductor and on the size and concentration of the particles.

Most of the scientific study of the colloidal colors has been concerned with relating the visual absorption spectrum of the glass to the optical properties of the colloid material and with studies of the nucleation and growth of the particles. The absorption spectrum can be calculated by applying the Mie's theory for the absorption of light by colloidal particles. Following equations are obtained by the surface plasmon resonace theory. The absorption coefficient is given by

Materials	Color	Materials	Color
Au	Ruby	Cu_2O	Ruby
Ag	Yellow	CdS	Yellow
Cu	Ruby	CdSe	Ruby
Se	Pink		

$$\alpha = [\,(18\pi NV\varepsilon^{2/3}\,)\,/\,\lambda\,]\,[\,\varepsilon/\,\{\,[\beta^2\,(\,\lambda - \lambda r\,) + \varepsilon_2{}^2]\}$$

$$\beta = |\partial\varepsilon_1\,/\,\partial\lambda|_{\lambda=\lambda c}, \quad \lambda = 2\pi C\varepsilon_m{}^{1/2}\,/\,\omega$$

and half height width is also expressed as

$$\Delta\lambda = \varepsilon_2\,/\,|\,\beta\,|$$

The yellow CdS and ruby CdSe colors are almost certainly due to colloidal particles. These glasses are of considerable technological interest because of the very sharp transmission cut-off in the blue part of the spectrum. Therefore, the color generation of semiconductor particles

Color	Composition	
	CdS %	CdSe %
Yellow	100	0
Orange	75	25
Red	40	10
Deep Red	10	90

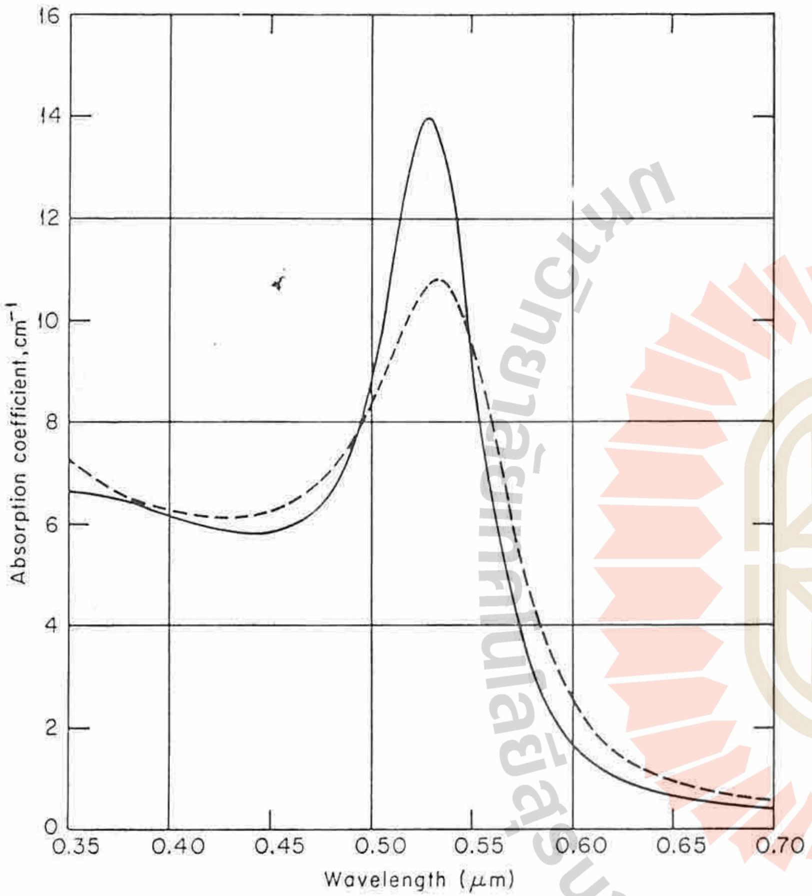


Fig. 35. Absorption spectrum of gold-ruby glass due to metal particles 200 Å in diameter in a photonucleated soda-alumino-silicate glass; (———) 25°C, (– – –) 514°C. (After Doremus, 1964.)

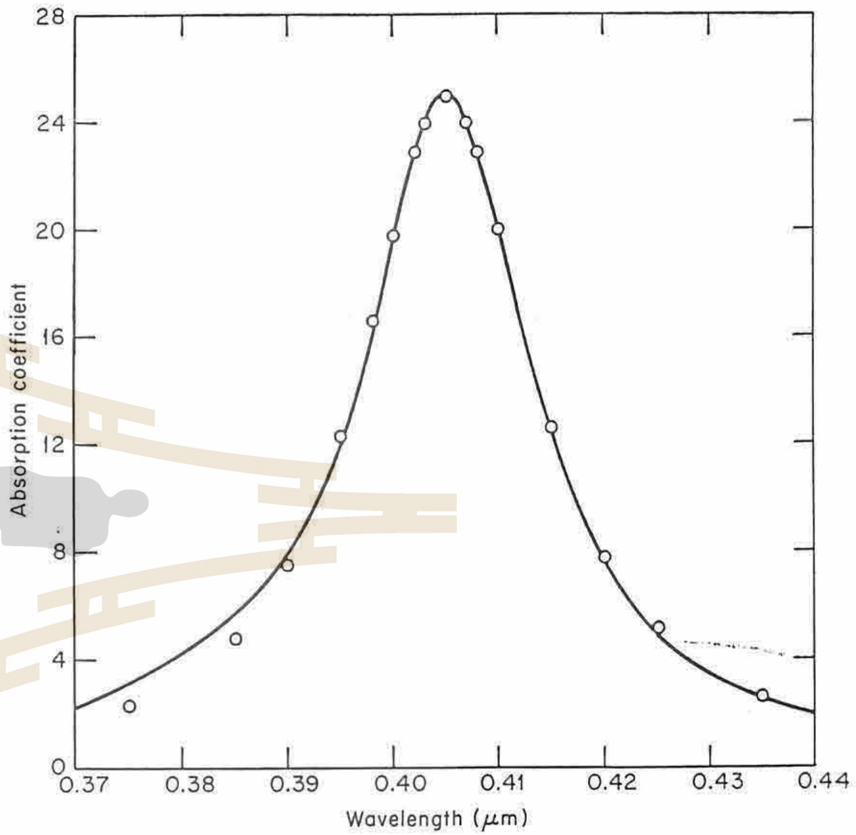
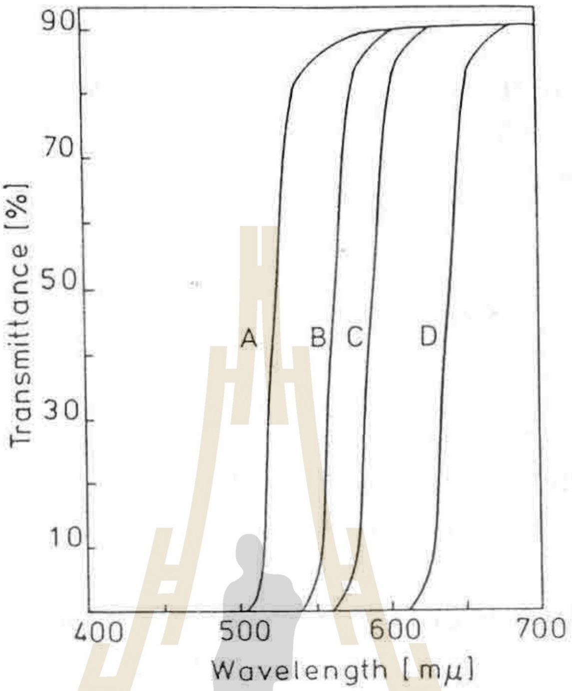


Fig. 36. Absorption spectrum of silver-yellow glass due to photonucleated metallic s particles [(——) experimental, (○) calculated. (After Doremus, 1965.)

is caused by band gap absorption



ig. 122. Curves of spectral transmittance of glasses ontaining CdS alone (A) and with increasing amounts of dSe (B,C,D). (Bausch and Lomb Inc.).

6. IR Absorption

The optical absoprtion of oxide glasses in the near and middle IR region is determined by the collective vibrations of molecules, atoms and ions in the glass network. Because of the complexity of the required calculations, no exact theory presently exists which satisfactorily describes the vibrational modes of a disordered system such as an oxide calculations, no exact theory presently exists which satisfactorily describes the vibrational modes of a disordered system such as an oxide glasses. Therefore, the absorption bands or peaks can be compared to that of crystals which have a known structure.

IR absorption is called Intrinsic, Eigen or Characteristic absorption. Absorption of IR occurs if the molecules have a dipole moment. Thus, the homomolecules such as O_2, N_2 has no vibrational IR spectrum. Typical stretching and bending vibrations are illustrated below.

stretching

bendinfg

(1). IR Cut-Off

For a simple atomic molecule, absorption of radiation may occur at the natural vibration frequency of the molecule. Assuming simple harmonic (natural) vibration:

○ ○
M_1 M_2

$$\nu_m = 1/2\pi C(k / \mu)^{1/2}$$

where μ is the reduced mass[Kg, $(M_1 \cdot M_2)/(M_1 + M_2)$, $1/\mu = 1/M_1 + 1/M_2$], ν_m is the vibrational frequency(cm^{-1}), k is the force constant(Nm^{-1}, $N = Kg \cdot m \cdot s^{-2}$, relates to the strength of chemical bond), and C is the velocity of light ($3\times10^8 m\cdot s^{-1}$).

According to this equation, we can estimate that what kind of

$\nu m \rightarrow$ Low Frequency $\rightarrow$ Longer Wavelength ($\nu m = 1/\lambda m$)

$\downarrow$

k $\rightarrow$ Smaller (Weaker Bond Strength)

μ $\rightarrow$ Larger (Heavier Mass of Elements)

materials can transmit IR radiation of longer wavelength.

k : Smaller

Covalent Bond> Ionic Bond> Van der Waals Bond

← stronger weaker →

← larger k smaller →

- Heavy alkali metal iodide (RI)

Example : CsI

$M_1 = 132.9\times10^{-3} / 6.023\times10^{-23} = 2.21\times10^{-25}Kg$

$M_2 = 126.9\times10^{-3} / 6.023\times10^{-23} = 2.11\times10^{-25}Kg$

$\mu = [(2.21\times 2.11)\times10^{-50}] / [(2.21 + 2.11)\times10^{-25}] = 1.08\times10^{-25}$

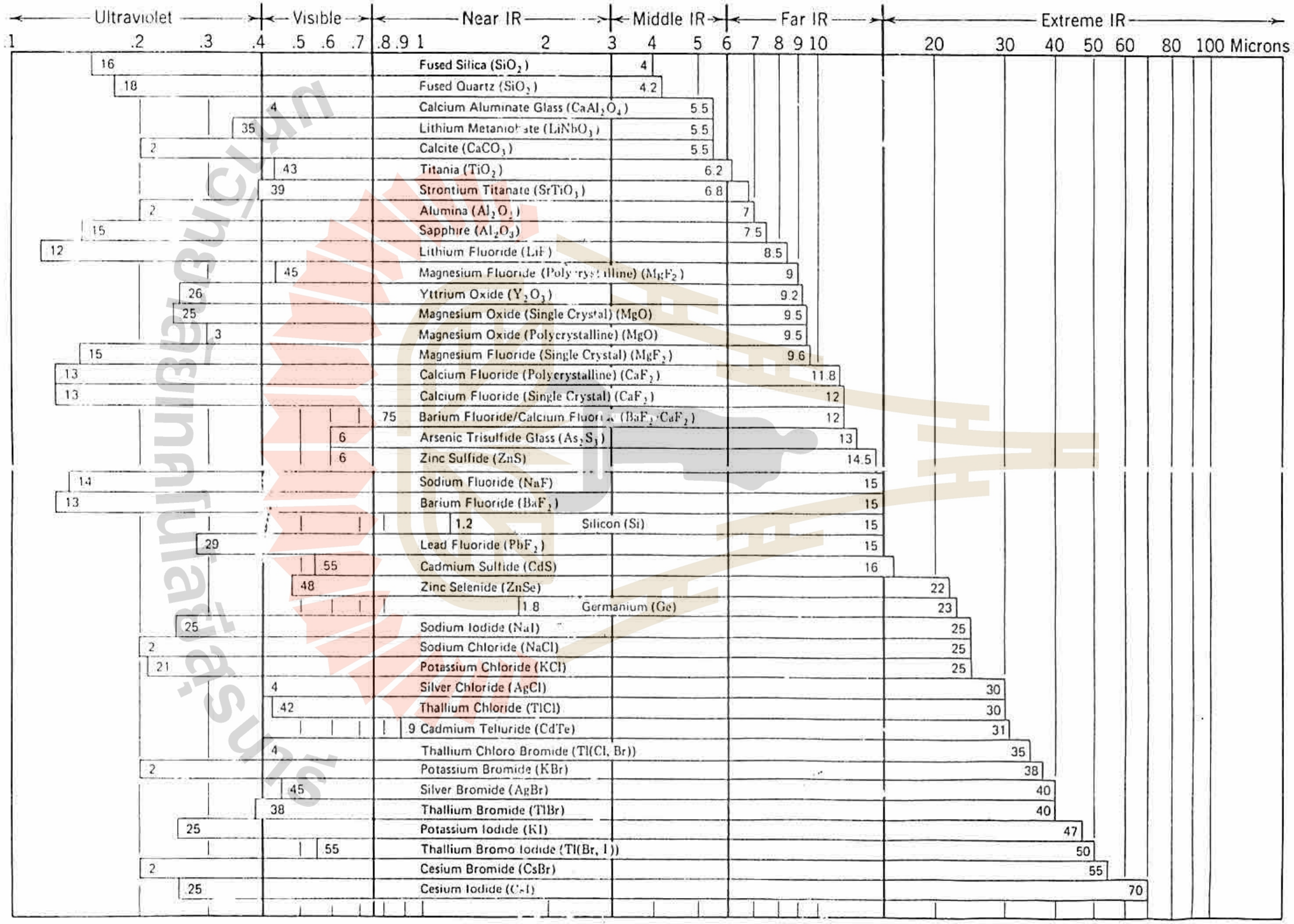
$k \approx 1\times 10^2 N/m$

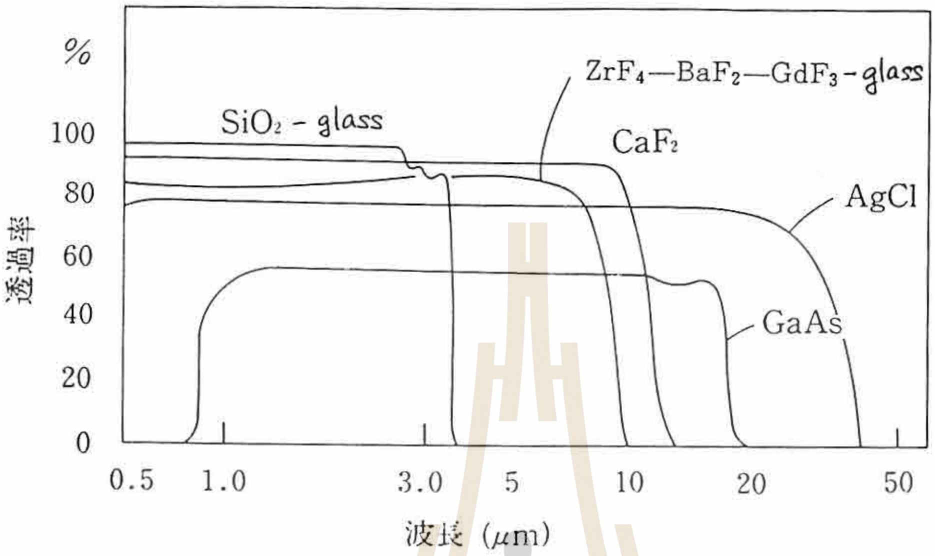
$\nu m = 5.3\times10^{-12}[(1\times10^2)/(1.08\times10^{-25})]^{1/2} = 1.61\times10^2 (cm^{-2})$

$* \ \lambda = 62 \ \mu m$

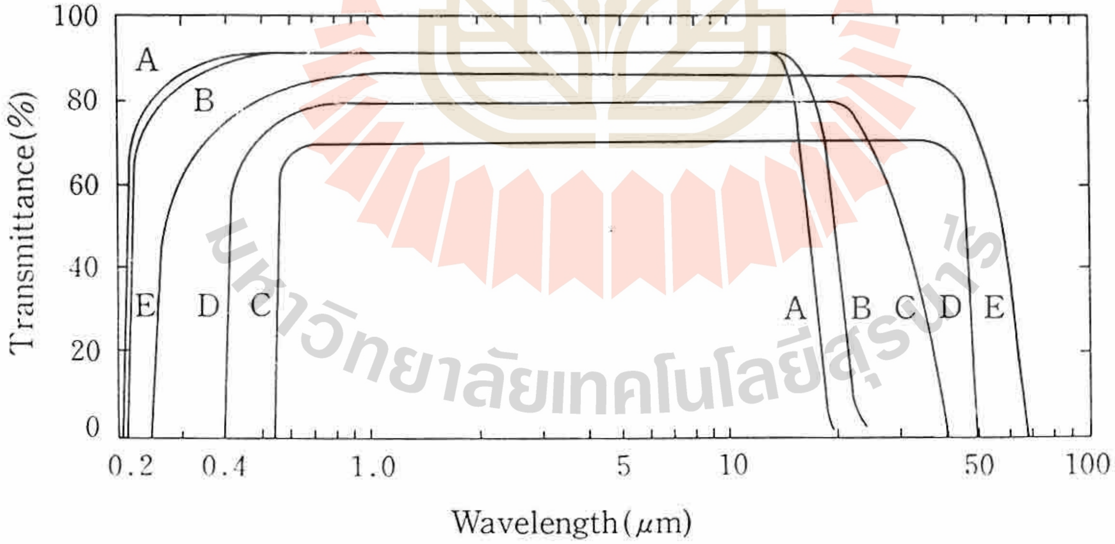
Actually, CsI crystal can transmit IR radiation of about 70μm (1 mm thick).

Table 13.1. Useful Transmission (Exceeding 10%) Regions of Materials for 2-mm Thickness





図－4　代表的な各種窓材料の透過率特性
（シリカガラス，フッ化カルシウム結晶，フッ化ジルコニウム系ガラス，
塩化銀結晶，ガリウムヒ素）



図－12　各種ハロゲン化物の透過特性
(A) NaCl, (B) KCl, (C) AgCl,
(D) KRS5 (TlBr+TlI), (E) CsI

(2). Compositional Effect

The bending vibrations are characterized by much lower frequencies than the stretching modes which involve larger force constants. The highest frequency vibrational modes of oxide glasses are associated with cation-oxygen stretching vibrations are quite sensitive to co-ordination and tend to more localized than the low-frequency modes. These high-frequency stretching modes to a great extent determine the IR Cut-Off wavelength of the glass. Some typical observed values of stretching frequencies in the glassy oxides are:

Si---O---Si : 1,100cm^{-1}
B---O---B : 1,250 "
P---O---P : 1,265 "
Ge---O---Ge : 900 "

IR absorption gives the structural information of glasses, hence the IR absorption method can be used for the structural analysis of glasses.

It is more difficult problem to predict theoretically the mode of vibration and the frequencies of atomic vibration of solids which have an infinite three-dimensional structure, unless the structure is a simple crystalline one. Only relatively recently have numerical calculations been carried out on the vibrational spectra of materials having non-periodic structures. Consequently much of the work which have been done in an attempt to interpret the IR spectra of oxide glasses has simply involved comparisons between the spectra of the glasses with those of crystalline compounds of known structure.

A good, relatively simple example of the use of an oxide glass is shown below for the crystalline and vitreous forms of GeO_2. In hexagonal GeO_2, X-ray structural studies have shown that the Ge atoms are surrounded by four oxygens at the center of an irregular tetrahedron. In the tetragonal form, the Ge atoms are surrounded by six oxygens. The IR spectrum of the glass, with its strongest absorption at 930cm^{-1} suggests that the glass structure is more similar to that of the hexagonal crystalline form, a suggestion which has been supported by X-ray studies of the glass structure.

The absorption spectra of silica shows a strong band at 1098cm^{-1} and somewhat weaker bands at 800cm^{-1} and 465cm^{-1}. The numerical studies of the vibration of the vitreous silica structure suggests that the band at 1098cm^{-1} is a bond stretching vibration, the other two being due to bond bending vibrations.

A particularly extensive study of the absorption spectra of R_2O-B_2O_3 glasses has been carried out. This is of particular interest for its use of comparisons with the spectra of crystalline borates to infer the structures

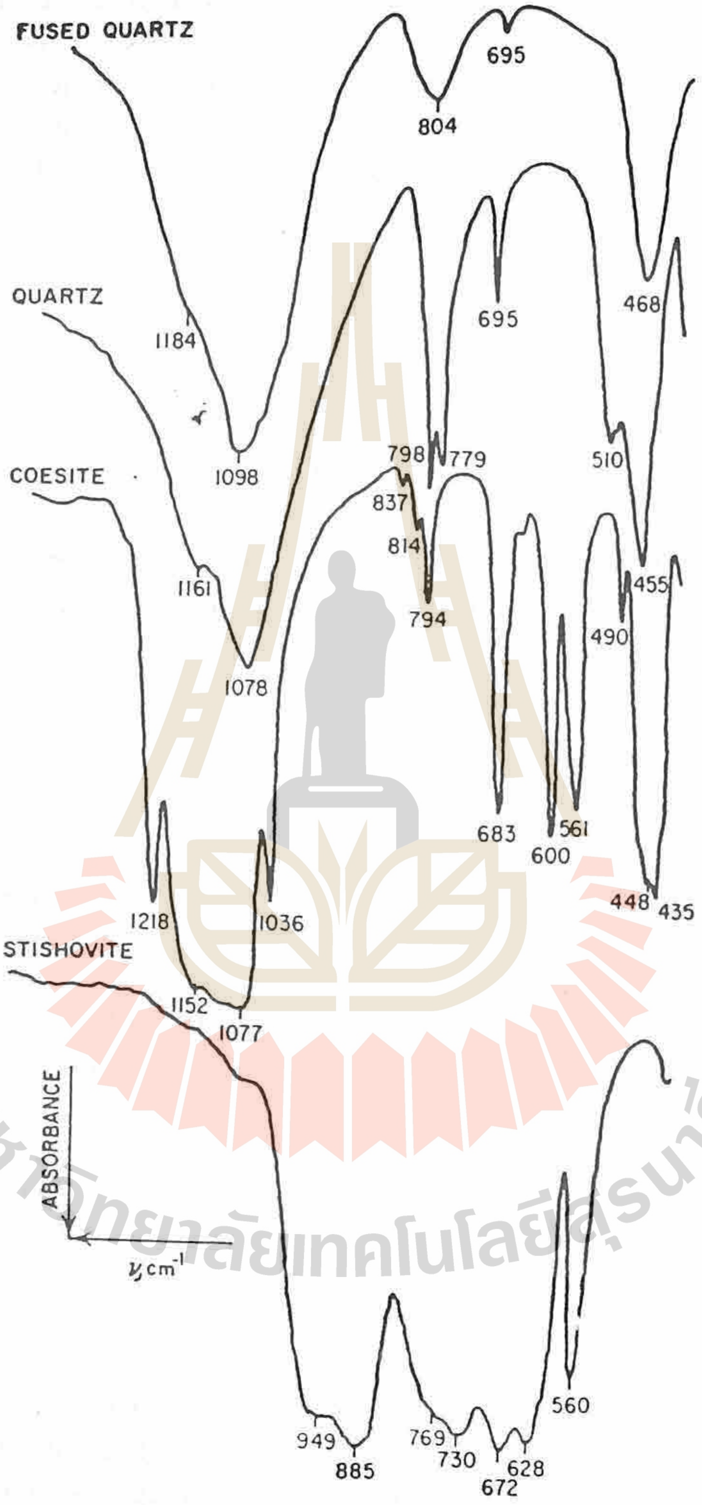


Fig. 40. Infrared absorption spectra of fused silica and three crystalline polymorphs. A change in the coordination of Si in stishovite (6-coordinated) produces a substantial shift in the Si–O stretching frequency, 1078–885 cm^{-1}. (After Lyon, 1962.)

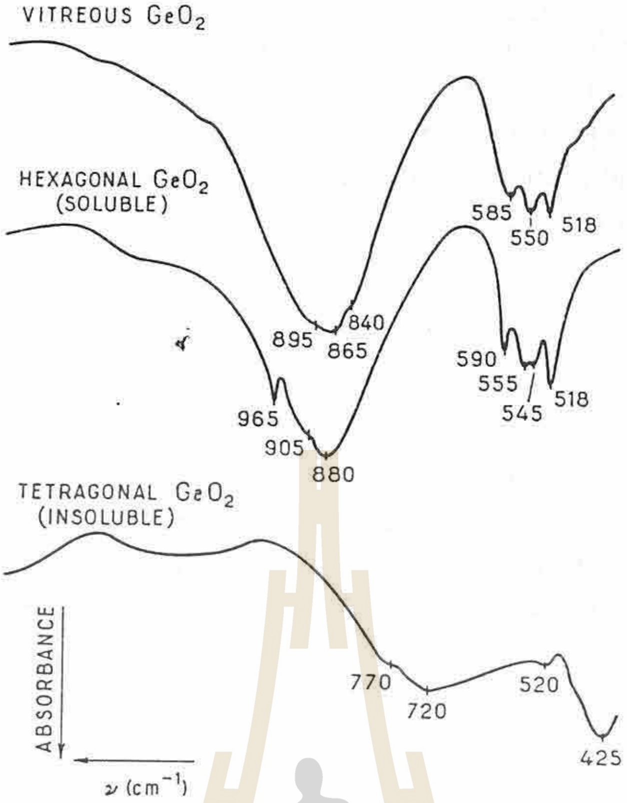


Fig. 48. Infrared absorption spectra of vitreous GeO_2, and the hexagonal (4-coordinated Ge) and tetragonal (6-coordinated Ge). The similarity of the glass to the hexagonal crystalline form is quite apparent. (After Zarcycki, 1964.)

which may be present in glasses.

One interesting system is the R_2O-Al_2O_3-B_2O_3 which have been measured using IR and Raman techniques. For compositions of $0.2K_2O$-$0.8B_2O_3$, the addition up to 20 mole % Al_2O_3 leads to decrease of absorption in the 900~1,100cm^{-1} region and an increase in the intensity of the 808cm^{-1}. Raman line, indicating that BO_4 units disappear and boroxol groups reform upon the addition of Al_2O_3. There is also evidence of AlO_4 tetrahedra formation when alkali oxide content exceeds 30 mole %.

7. Electro-Optic and Acoust-Optic Materials

Systems based on laser technology will require much additional hardware in addition to the lasers and wave guides. For example, devices will be required to modulate, switch, deflect, translate in frequency, and otherwise modify the optical signal in a predictable and controllable manner. Needs in this area have prompted the development of materials which are capable of optical transmission with low loss, which have optical properties that can modified by electric or magnetic field or by extremely applied stresses, and whose properties will interact in a specified manner with the optical signal. Important among these are the so-called electro-optic and acoust-optic glasses.

(1). Electro-Optic Glasses

The electro-optic effect occurs whenever an applied electric field produces a change in the optical dielectric properties. When the polarized light are incident upon the substances, which are placed in parallel to the magnetic field, the plane of polarized light can rotates by Faraday Effect. The angle of rotation is given by

$$\theta = VHL$$

where V is Verde constant (degree(min.)/ Oe·cm), H the strength of magnetic field(Gauss) and L the length of substance(cm).

The glasses having a large V values is called Faraday rotation glasses, and applied for opt-isolator and the sensors of electric-magnetic field measurement. Below figure shows the principles of opt-insulator.

Diamagnetic glasses have a positive Verde constant, its value can be expressed by

$$V = (\nu g/2mc^2)(dn/d\nu)$$

where ν is a frequency of light, n the refractive index, g the Rand constant. $d\nu/dn$ indicates the dispersion of refractive index, the glasses containing Pb^{2+}, Bi^{3+} and Te^{4+}, which have the large dispersion, have a large Verde constant. A paramagnetic glasses containing rare earth ions, which have unpaired electrons, has a negative Verde constant and is expressed by

$$V = [16\pi^2\mu_B\nu^2/3chkT][(NP/g)\Sigma[Cn/(\nu^2 - \nu^2)]]$$

where μ_B is the number of Bohr magnet, h Plank constant, T the temperature. N the number of diamagnetic ions, P the the number of effective magnet. ν the characteristic absorption frequency and Cn the transition probability.

The capability of Faraday rotation glasses is determined by the V/α, α is the absorption coefficient. Although the large glasses can be produced, the Verde constant is much smaller than that of crystal.

(2). Acoust-Optic Glasses

Change in the refractive index of glasses can also be induced by strain. The strain acts to alter the internal potential, and this changes the shape and sizes of the orbitals of the weakly bound electrons and hence causes changes in the polarizability and refractive index.

When the ultrasonic wave are incident upon the transparent materials, the periodic changes of the refractive index generates, and this deflects the light as a diffraction grating. The strength of diffracted light can be expressed by

$$I = Io\ \mathrm{Sin}^2(K\cdot Me\cdot Ps/\lambda)^{1/2}$$

where Io is the intensity of incident light, K the constant, Ps the intensity of ultrasonic wave, λ the wavelength of light. Me is the measure of ultrasonic materials, is given by

$$Me = n^6P^2/\rho v^2$$

where n is the refractive index, P the opt-electric constant, ρ the density of glass and v the velocity of sound. Me depends on the refractive index, high-PbO-glass or tellurite glasses which have high refractive index and lower velocity of sound, is required.

PbO glasses can be used in below 100MHz because the high absorption of ultrasonic wave.

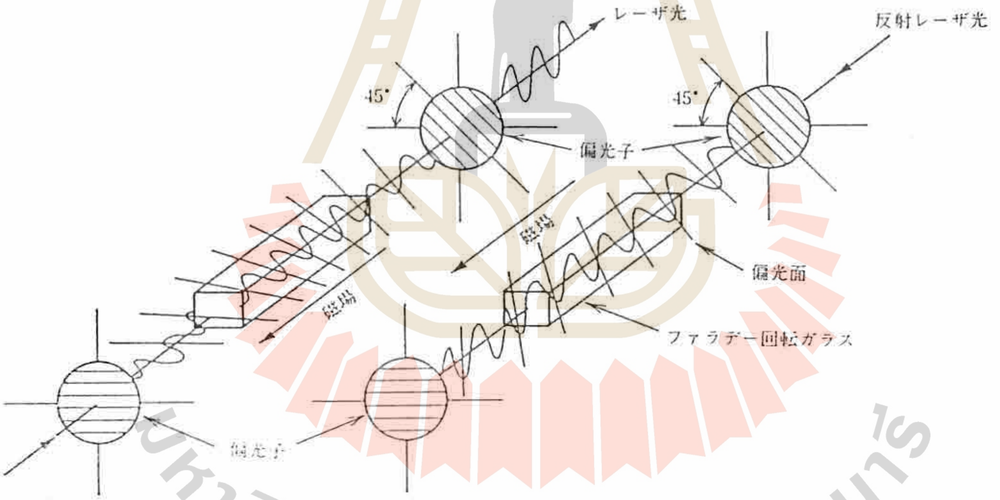


図 18 光アイソレータの原理

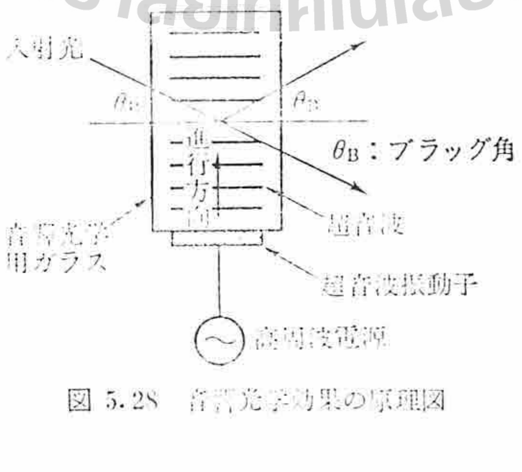


図 5.28 音響光学効果の原理図

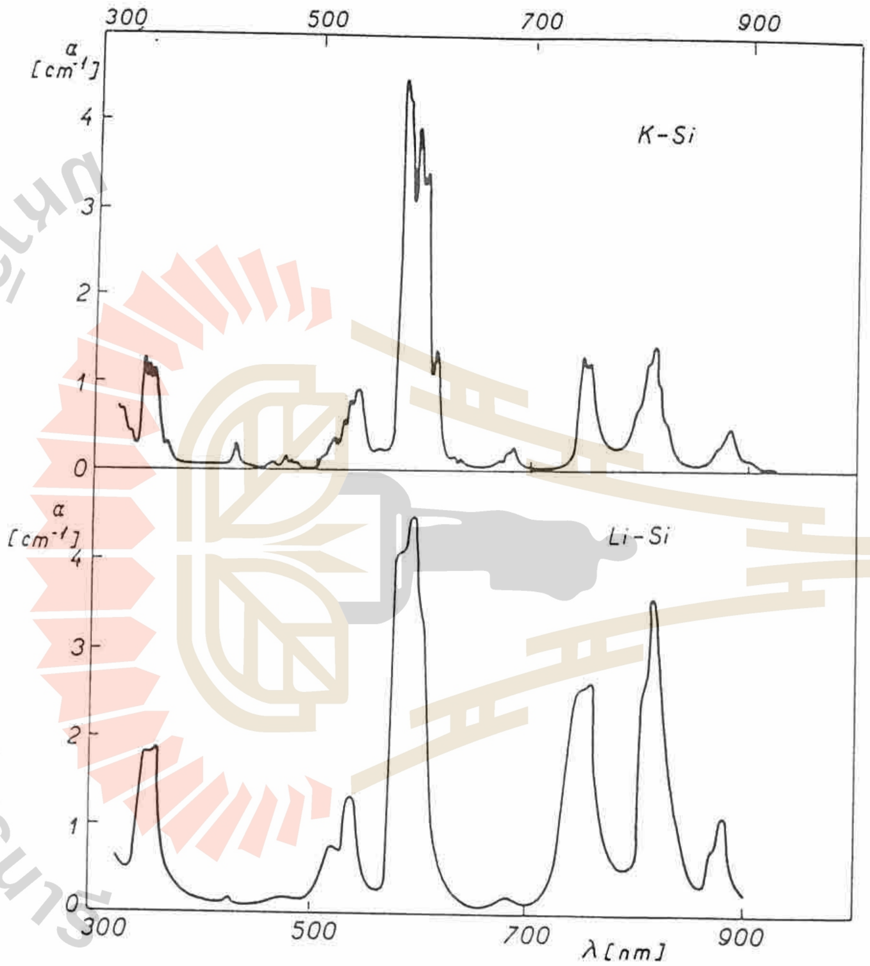


Fig. 33. Comparison of the optical absorption spectra of Nd^{3+} in different host glasses. Ligand field interactions with the 4f electrons are weak so that spectral features of trivalent rare earth ions are similar in all hosts. (After Patek, 1970.)

IX. Refractive Index and Dispersion of Glass

1. Refractive Index

A dielectric material, such as glass and ceramics, reacts to electromagnetic radiation differently from free space because it contains electrical charges that can be displaced.

Fig. 13.8. Shift of electron cloud giving rise to dipole moment and electronic polarization.

For a sinusoidal electromagnetic wave, there is a change in wave velocity and intensity described by the complex coefficient of refraction:

$$n^* = n - ik$$

where n is the index of refraction and k is the index of absorption. The coefficient of refraction is related to the complex dielectric constant, $n^{*2} = \varepsilon^*$. Since $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' is the relative dielecric constant and ε'' is the relative dielecric loss factor,

$$n^{*2} = n^2 - k^2 - 2ink$$
$$\varepsilon' = n^2 - k^2 \quad \varepsilon'' = 2nk$$

(1). Definition

When light passes from a vacuum into denser material, its velocity is decreased. The ratio between these velocities determines the index of refraction n:

$$n = C_{vacuo} / C_{material}$$

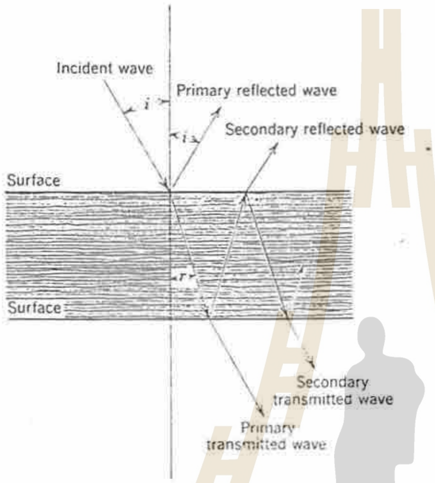
The relative index of refraction between phases (ratio of refractive index) determines the reflectance and refractive properties of a phase boundary. The change in velocity causes light to bend of incidence from a normal to the surface i and the angle of refraction is r, these angle are related, when one medium is air or vacuo, by

$$n = \sin i / \sin r \quad \text{(Snell' Law)}$$

On the contrary, when the light passes from a denser material to vacuo or air, the light can be reflected entirely, if the incident angle i is greater than specified angle i'. This specified angle I' is called critical angle, and is given by

$$\mathrm{Sin}\ i = n' / n$$

where i' is a critical angle, n' is a refractive index of air or vacuum, and n is a refractive index of materials. If n =1.5, i is given by 41.8°.



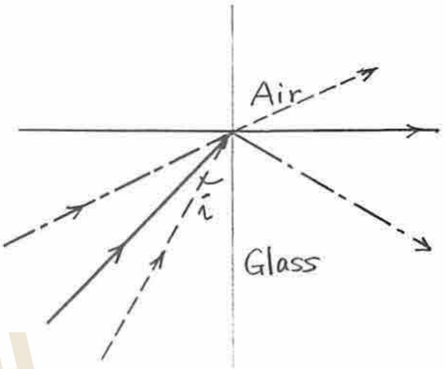


Fig. 13.5. Reflection and transmission of light by a sheet of material.

(2). Polarizability and Molar Refractivity

A dielectric material reacts with and affects electromagnetic radiation because it contains charged carriers that can be displaced. The light waves are retarded because of the interaction of the electromagnetic radiation and the electronic systems of the atoms. The relationship

between the applied field and medium can be considered as resulting from the presence of elementary electric dipoles having an average dipole moment μ. If the dipole is represented by two charges of the opposite polarity, + and –Q, separated by the distance d, then μ=Qd. Over the range of optical frequencies the source of this dielectric polarization is the shift of the electron cloud around the atomic nucleus.

The average dipole moment μ is proportional to the local electric field strength that acts on the particles; the proportionality constant α is called polarizability and measures the average dipole moment per unit field strength, $\mu = \alpha E$. The summation of all elementary dipoles gives the total dipole moment per unit volume or the polarization P: that is, if there are N particles per unit volume,

$$P = N\mu = N\alpha E$$

the Lorentz-Lorenz equation, connects the polarizability α of the atoms of an elementary monatomic gas with

$$\alpha = (3\varepsilon_o / 4\pi)\cdot[(\varepsilon - \varepsilon_o)/(2\varepsilon_o+\varepsilon)]\cdot M/\rho = R\cdot(3\varepsilon_o/4\pi)$$

$$\therefore R = [(\varepsilon - \varepsilon_o)/(2\varepsilon_o+\varepsilon)]\cdot M/\rho = [(n^2-1)/(n^2+2)]\cdot M/\rho$$

where M is the molar weight, ρ is the density and R is the molar refractivity and is directly proportional to the atomic and ionic refractivities.

$$R = \Sigma\, Ri\cdot Xi$$

In most glasses, the largest contribution to the molar refractivity of the glass comes from the oxygen ion. A few simple calculations are sufficient to show that the oxygen ion refractivity is not constant. It depends on whether the oxygen is bridging or non-bridging and it is also affected by the proximity of other cations. Ionic or atomic refractivities is shown (table). For example, in SiO_2 glass has a molar refractivity of R_M=7.44 cm^3, its oxygen ion refractivity is given by Roxy=(7.44 – 0.10)/2=3.67 cm^3.

(3). Refractive Index Measurement

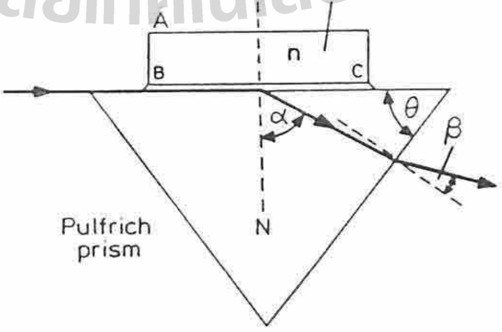


Fig. 85. Pulfrich refractometer.

When and accuracy of one or two units in the fourth decimal place is sufficient, use of commercial Pulfrich Refractometer is the most widely used method. This instrument depends on the measurement of critical angle of refraction. By applying Snell's law, the refractive index n of glass specimen can be calculated by

$$n=\mathrm{Sin}\theta\cdot(N^2-\mathrm{Sin}^2\beta)^{1/2}+\mathrm{Cos}\theta\cdot\mathrm{Sin}\beta$$

If a higher accuracy is required, with results accurate to one or two units in the fifth or even the sixth decimal place, it is necessary to use a high precision spectrometer, or V-block refractometer.

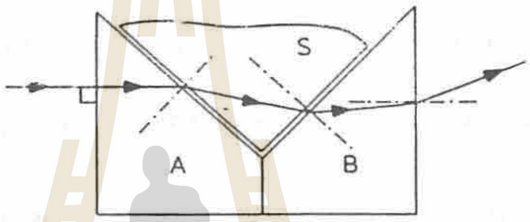


Fig. 86. V-block refractometer.

In optical glass catalogues, values of refractive index are quoted at a number or wavelengths corresponding to lines in the emission spectra of certain elements. These spectral lines are denoted by lower and upper case letter symbols which are used as suffixes to denote the wavelength at which a property is specified. Thus n_d represents the refractive index measured using the yellow helium line at 587.56nm.

TABLE XVII

Spectral lines commonly used for refractive index measurement.

Symbol	Wavelength nm	Element	Colour
i	365.01	Hg	UV
h	404.66	Hg	Violet
g	435.84	Hg	Blue
F´	479.99	Cd	Blue
F	486.13	H	Blue
e	546.07	Hg	Green
d	587.56	He	Yellow
D	589.29	Na	Yellow
C´	643.85	Cd	Red
C	656.27	H	Red
r	706.52	He	Red
s	852.11	Cs	Infra-red
t	1013.98	Hg	Infra-red

TABLE XV

The refractivities of ions

Ion	R_I cm^3
F^-	2.5
Cl^-	9.00
Br^-	12.67
I^-	19.24
Li^+	0.20
Na^+	0.50
K^+	2.23
Cs^+	6.24
Be^{++}	0.10
Mg^{++}	0.28
Ca^{++}	1.33
Ba^{++}	4.30
Pb^{++}	3.10
B^{3+}	0.05
Al^{3+}	0.17
Si^{4+}	0.10
P^{5+}	0.07

TABLE XVI

Refractivities of oxygen anions in crystalline orthosilicates

Material	$R_{I,O}$ cm^3
25% Na_2O.75% SiO_2 glass	4.72
Mg_2SiO_4 crystal	3.83
Ca_2SiO_4 crystal	4.53
Sr_2SiO_4 crystal	4.67
Ba_2SiO_4 crystal	4.97

Table 13.2. Molar Refractivities of a Number of Atoms and Ions

Number of Electrons	Charge					
	−2	−1	0	+1	+2	+3
10	O	F	Ne	Na	Mg	–
	7.0	2.4	1.0	0.5	0.3	
18	–	Cl	A	K	Ca	Sc
	–	9.0	4.2	2.2	1.3	0.9
36	–	Br	Kr	Rb	Sr	-
	–	12.6	6.3	3.6	2.2	
54	–	I	Xe	Cs	Ba	La
		19.0	10.3	6.1	4.2	3.3

Molar Volume, Molar Refractivity and Ionic Refractivity of Oxygen Ion

Glass	Density (g/cm^3)	Refractive Index	Molar Volume (cm^3/mole)	Molar Refractivity (cm^3/mole)	Ionic Refractivity of Oxygen(cm^3)
SiO_2	2.20	1.458	27.30	7.449	3.675
$Li_2O{\cdot}4SiO_2$	2.283	1.500	23.664	6.960	3.778
$Na_2O{\cdot}4SiO_2$	2.391	1.490	25.281	7.309	3.905
$K_2O{\cdot}4SiO_2$	2.394	1.495	27.939	8.148	3.987
$Rb_2O{\cdot}4SiO_2$	2.890	1.504	29.564	8.754	4.019
$Cs_2O{\cdot}4SiO_2$	3.268	1.526	31.950	9.807	4.048

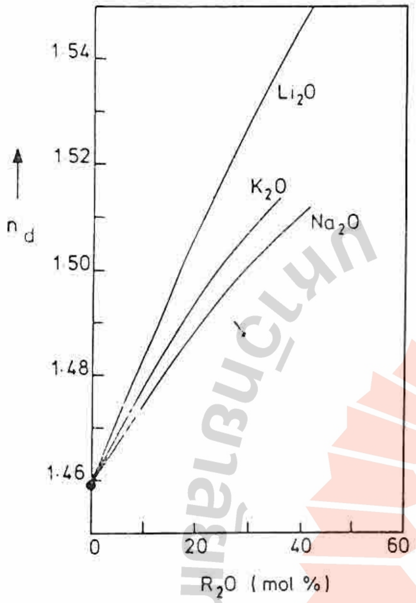
Table 13.3. Refractive Indices of Some Glasses and Crystals

	Average Refractive Index	Birefringence
Glass composition:		
From orthoclase ($KAlSi_3O_8$)	1.51	
From albite ($NaAlSi_3O_8$)	1.49	
From nepheline syenite	1.50	
Silica glass, SiO_2	1.458	
Vycor glass (96% SiO_2)	1.458	
Soda-lime-silica glass	1.51–1.52	
Borosilicate (Pyrex) glass	1.47	
Dense flint optical glasses	1.6–1.7	
Arsenic trisulfide glass, As_2S_3	2.66	
Crystals:		
Silicon chloride, $SiCl_4$	1.412	
Lithium fluoride, LiF	1.392	
Sodium fluoride, NaF	1.326	
Calcium fluoride, CaF_2	1.434	
Corundum, Al_2O_3	1.76	0.008
Periclase, MgO	1.74	
Quartz, SiO_2	1.55	0.009
Spinel, $MgAl_2O_4$	1.72	
Zircon, $ZiSiO_4$	1.95	0.055
Orthoclase, $KAlSi_3O_8$	1.525	0.007
Albite, $NaAlSi_3O_8$	1.529	0.008
Anorthite, $CaAl_2Si_2O_8$	1.585	0.008
Sillimanite, $Al_2O_3{\cdot}SiO_2$	1.65	0.021
Mullite, $3Al_2O_3{\cdot}2SiO_2$	1.64	0.010
Rutile, TiO_2	2.71	0.287
Silicon carbide, SiC	2.68	0.043
Litharge, PbO	2.61	
Galena, PbS	3.912	
Calcite, $CaCO_3$	1.65	0.17
Silicon, Si	3.49	
Cadmium telluride, CdTe	2.74	
Cadmium sulfide, CdS	2.50	
Strontium titanate, $SrTiO_3$	2.49	
Lithium niobate, $LiNbO_3$	2.31	
Yttrium oxide, Y_2O_3	1.92	
Zinc selenide, ZnSe	2.62	
Barium titanate, $BaTiO_3$	2.40	

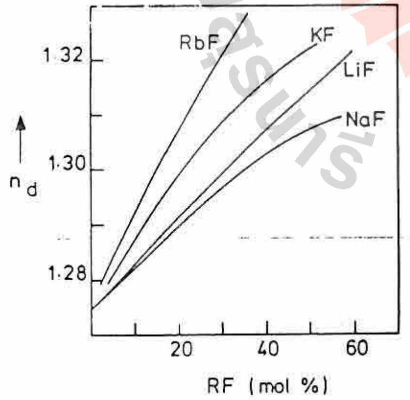
TABLE XIV

Refractive index n_d at λ = 587.6 nm of some one-component glasses and inorganic compounds

	Glasses	n_d
	BeF_2	1.275
	B_2O_3	1.458
	SiO_2	1.458
	GeO_2	1.607
	Crystals	
SiO_2:	α-Quartz	1.544-1.553
	Tridymite	1.469-1.473
	Cristobalite	1.484-1.487
	LiF	1.392
	NaF	1.325
	NaCl	1.550
	KCl	1.490
	KBr	1.560
	MgO	1.737
	Diamond	2.419



g. 87. Effect of composition on the refractive index of asses in the systems R_2O-SiO_2 (Vogel and Gerth, 1958).



g. 88. Effect of composition on the refractive index o asses in the systems RF-BeF_2. (Vogel and Gerth, 1958).

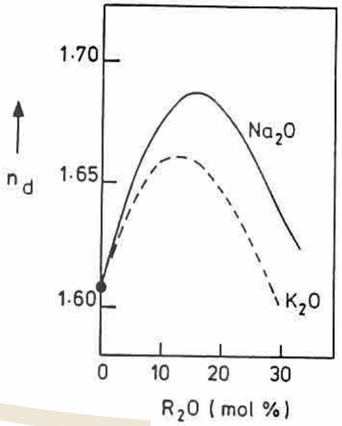


Fig. 89. Effect of composition on the refractive index of glasses in the systems R_2O-GeO_2.

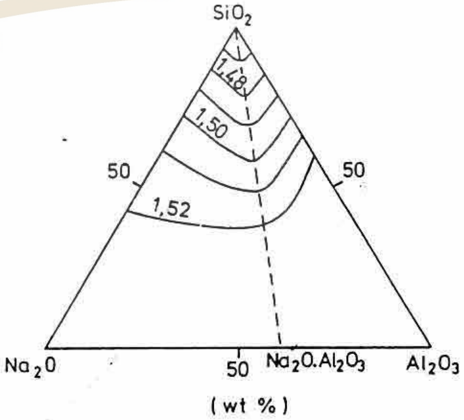


Fig. 90. Effect of composition on the refractive index of glasses in the system Na_2O-Al_2O_3-SiO_2.

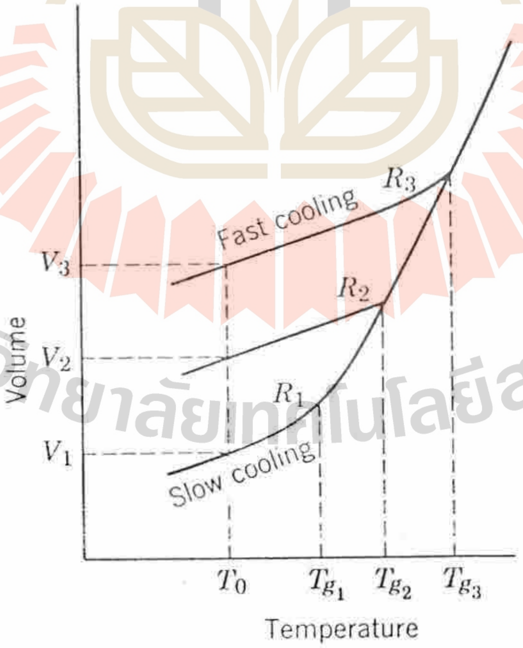
(4). Effect of Glass Composition

Vitreous BeF_2 has probably the lowest refractive index of the inorganic glasses. Most oxide glasses have refractive indices between 1.45 and 2.0, but new oxide glasses have been discovered containing compositions for which the refractive indices are higher, e.g. the tellurite glasses with values as high as 2.3 - 2.4. The chalcogenide glasses have higher values still.

In many two-component glass systems, e.g. alkali silicate system, the refractive index varies almost linearly with composition. However, there are other systems in which the composition dependence shows interesting departures from linearity. These have been interpreted in terms of changes in the coordination number of the network forming cations. Boric oxide anomaly, germania anomaly, and alumina anomaly has been observed in $R_2O(RO)$-B_2O_3, $R_2O(RO)$-GeO_2, and Na_2O-Al_2O_3-SiO_2 glass systems respectively.

(5). Effect of Heat Treatment

General features of the properties of glass is that measurements made below the transformation range, e.g. at room temperature, are affected by the previous heat treatment, especially that given whilst the glass was in, or as it passed through the transformation range. Thus a glass which has been rapidly cooled from a high temperature has a lower density than the same material when cooled slowly. The more rapidly cooled glass has a higher fictive temperature: its configuration corresponds to that in equilibrium at a higher temperature. As has been shown above, the



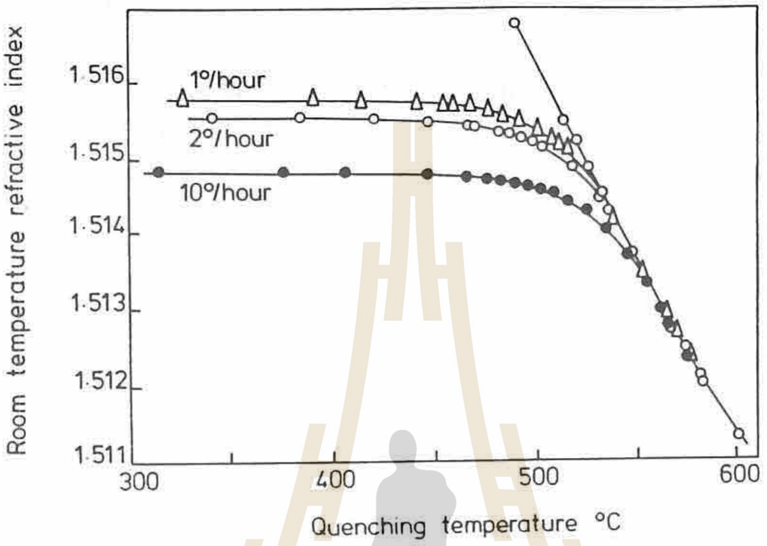


Fig. 92. Effect of quenching temperature on the room-temperatur of refractive index of a borosilicate optical glass.

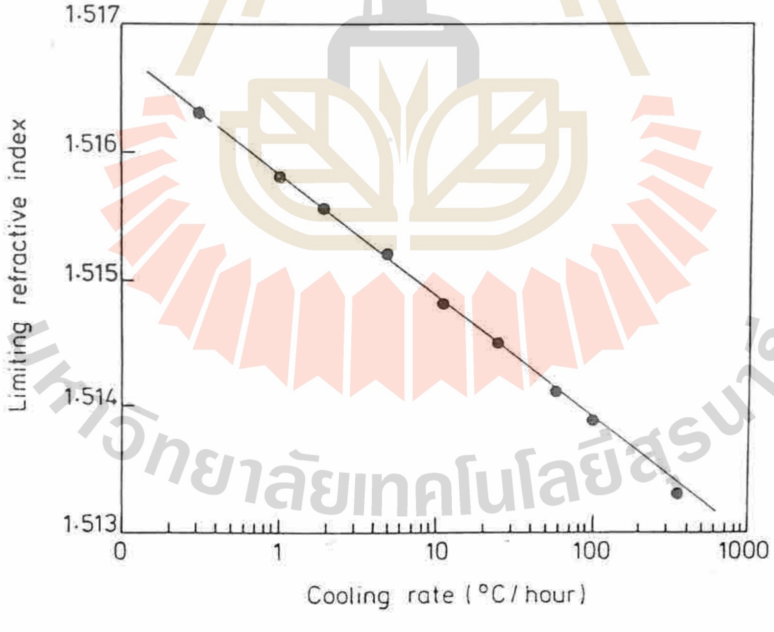


Fig. 93. Effect of cooling rate on the refractive index of samples cooled continuously to room temperature.

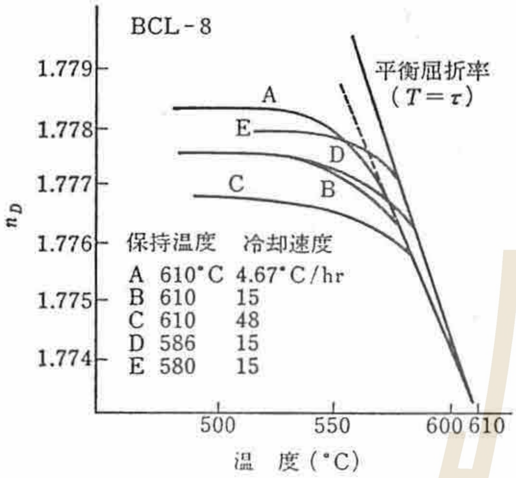


図 3.32　定速冷却時の屈折率変化

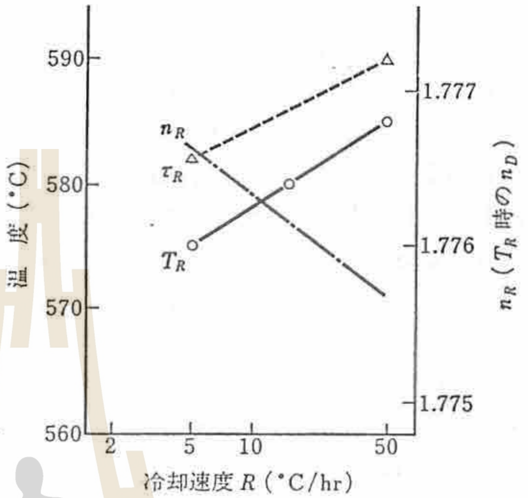


図 3.33　冷却速度と T_R, τ_R, n_R の関係(BCL8)

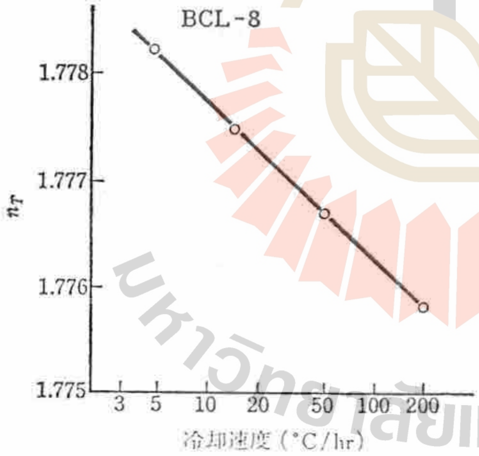


図 3.36　n_T と冷却速度の関係

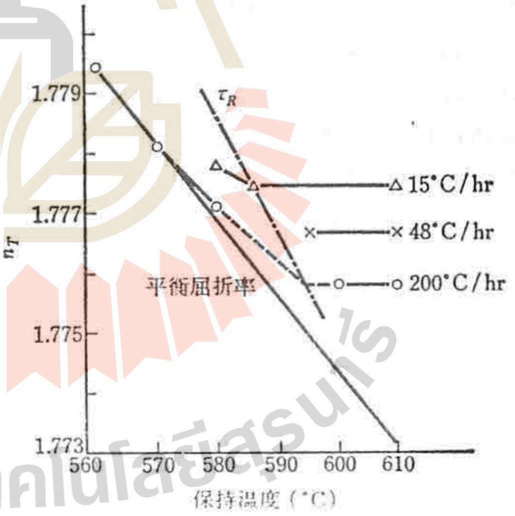


図 3.37　n_T と保持温度の関係 (BCL8)

refractive index of material is affected by density. It is not surprising therefore that this property is also affected by cooling rate: the higher the cooling rate through the transformation range, the lower the refractive index.

Because of the precise refractive index control to the optical glass industry a number of thorough studies have been made on the effect of heat treatment on refractive index.

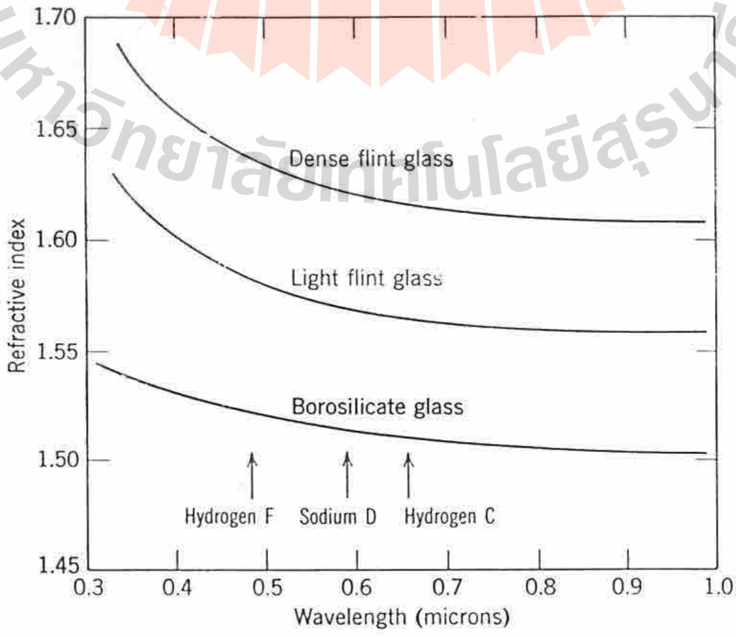
For the continuously cooled specimens, the slower the rate of cooling, the lower the temperature at which the glass is able to attain the equilibrium configurations during the cooling period.

The effect of cooling rate on the refractive index is very large in relation to the degree of reproducibility demanded for high quality optical glass. It is therefore necessary to control the heat treatment very carefully indeed to ensure that different parts of the same block of optical glass experience a very similar temperature-time schedule. The requirements for optical annealing to obtain a uniform refractive index through the material are much more stringent than that of merely ensuring that the dis-annealing stress in the material below a specified level. A very low level of stress in optical glass is also of course necessary since stress affects the refractive index and makes the material birefringence.

1. Dispersion

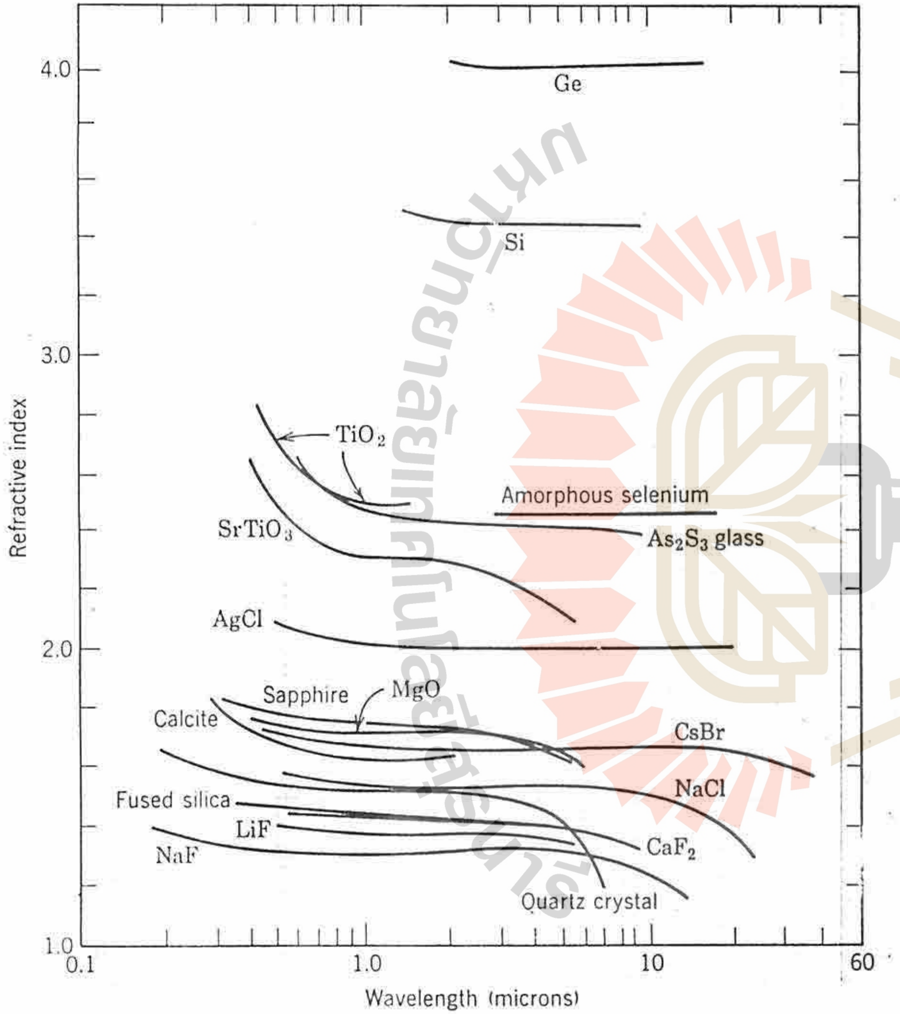
(1). Definition

The refractive index is a function of the frequency of the light, normally decreasing as the wavelength increases. This change with wavelength is known as dispersion of the refractive index and has been defined in various ways. At any wavelength of interest the dispersion can be most directly given by



(*a*)

Fig. 13.3. (*a*) Change in refractive index with wavelength for typical glasses in the visible



(*b*)

Fig. 13.3 (*Continued*). (*b*) Change in refractive index with wavelength for several crystals and glasses.

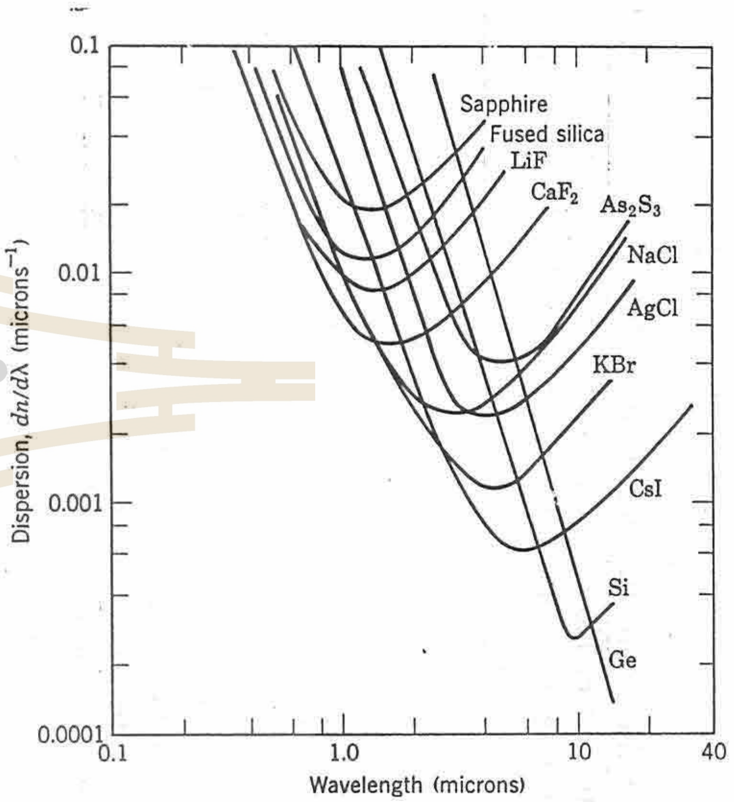


Fig. 13.4. Dispersion as a function of wavelength for several ceramics shown in Fig. 13.3*b*.

$$\text{Dispersion} = dn/d\lambda$$

and this value can be determined directly from refractive index-wavelength curve. However, most practical measurements are made by using the refractive index at fixed wavelength rather than determining the complete dispersion curve.

(2). Origin of Dispersion : Lorentz Theory

The dispersion of the refractive index results from the fact that the visible spectrum is adjacent to the natural frequency of electronic oscillators in the ultraviolet. There is strong interaction with electromagnetic radiation of the natural frequency causing resonance, or reinforcement of the natural oscillators, and a high absorption at this resonant frequency. Results for glasses of simple composition are quoted which illustrate this dependence. It is then possible to look at the compositions of commercial optical glasses with some understanding of how their compositions affect their optical properties. A brief consideration of the problem of designing compound lenses to minimize aberrations is used to explain why it is necessary to manufacture such a wide range of optical glass compositions.

The simple classical model of Lorentz gives the adequate qualitative picture of the phenomenon of dispersion.

Here, we describe the physical basis of the model and quotes equations derived from it.

The model pictures the material as consisting of electrons to equilibrium positions by linear forces, i.e., if an electron is displaced from its equilibrium position by a distance x, it experiences a force ax acting to restore it position. It is assumed that each electron is also subjected to a damping force, which is proportional to its velocity dx/dt. If the electrons are subjected to the alternating electric field of a light wave of $E(=E_0 e^{i\omega t})$, they vibrate in response to the field. The equation of motion of electrons is therefore

$$m \cdot dx^2/dt^2 + b \cdot dx/dt + ax = eE$$

if, b(measure the damping constant) is small and outer force can be zero, its oscillates naturally, and its natural frequency is ω_o,

$$\omega_o = (a/m)^{1/2}$$

and b=mg, the above equation is expressed by

$$m\cdot dt^2/dx^2 + mg\cdot dx/dt + m\cdot\omega_o^2 x = eE$$

Furthermore, E can be expressed by the real part of $E = E_o e^{i\omega t}$ and also x can be expressed by the real part of $x = x_o e^{i\omega t}$,

$$X = [(e/m)]/[\omega_o^2 - \omega^2 + i\omega g]$$

This equation indicates that the electrons vibrates of frequency same as that of applied electrical field and that amplitude changes with frequency. Here, assuming Nk electrons having ωk and gk, the total polarization P is given by

$$P = E\,\Sigma\ \{[N_k e^2/m]/[\omega_k^2 - \omega^2 + i\omega g_k]\}$$

Therefore the dielectric constant ε is given by

$$\varepsilon = 1 + \Sigma\ \{[N_k e^2/m]/[\omega_k^2 - \omega^2 + i\omega g_k]\}$$

At the constant frequency ωk, dielectric constant changes abruptly, and absorption and dispersion would take place. Absorption coefficient is defined as

$$\gamma = i\omega(n - ik)/c,\quad \exp(-\gamma z) = \exp(-\omega/c)kz\cdot\exp[-I(\omega/c)nz]$$

and

$$(n - ik)^2 = \varepsilon$$

Finally,

$$(n - ik) = 1 + 1/2\{\Sigma\{\,[N_k e^2/m\varepsilon_o]/\,[\omega_k^2 - \omega^2 + i\omega g_k]\}$$

then

$$\mathrm{Re}\{\varepsilon\} = n = 1 + 1/2\Sigma\{(N_k e^2/m\varepsilon_0)\cdot(\omega_k^2 - \omega^2)/[(\omega_k^2 - \omega^2)^2 + \omega^2 g_k^2]\}$$

$$\mathrm{Im}\{\varepsilon\} = k = 1/2\Sigma\{\,(N_k e^2/m\varepsilon_o)\omega g_k/[(\omega_k^2 - \omega^2)^2 + \omega^2 g_k^2]\}$$

On the other hand, in the liquid or solid, the applied force for the electrons is not only by the applied field but also by the polarization of surroundings. In this case, the polarization for liquid and solid is given by

$$P = (E + P/3\varepsilon_o)\cdot\Sigma[(Nke^2/m)/(\omega k^2 - \omega^2 + i\omega gk)]$$

$$D = \varepsilon\cdot\varepsilon_o E = \varepsilon_o E + P$$

$$E + P/3\varepsilon_o = [(\varepsilon + 2)/3]E$$

Therefore, ε is given by

$$(\varepsilon-1)/(\varepsilon+2) = [(n-ik)^2 - 1]/[(n-ik)^2 + 2] =$$
$$1/3\ \Sigma[(Nke^2/m_o\varepsilon_o)/(\omega k^2 - \omega^2 + i\omega gk)$$

and Nk can be replaced by *f*kN, and the above equation can be written as

$$[(n-ik)^2 - 1]/[(n-ik)^2 + 2] = 1/3\ \Sigma[(fke^2/m_o\varepsilon_o)/(\omega k^2 - \omega^2 + i\omega gk)$$

*f*k is called oscillator intensity. For the transparent materials, the damping factor gk can be neglected, and for the light of constant wavelength, the next equation is obtained(Lorentz-Lorenz Equation).

$$[(n^2 - 1)/(n^2 + 2)](1/\rho) = \text{Constant}$$

The equation of a motion of electrons is given by

$$md^2x/dt^2 + mgdx/dt + m(\omega\varepsilon_o{}^2 - Ne^2/3\varepsilon_o m)x = eE$$

By solving above equation, therefore

$$(n - ik)^2 = 1 + (Ne^2m_o)/(\omega_o{}^2 - \omega^2 + i\omega g)$$

and the resonant frequency can be given by

$$\omega_o{}^2 = \omega_o{}^2 - (Ne^2/3\varepsilon_o m)$$

From this equation, while the abnormal dispersion takes place similarly to gas, the resonant frequency differs from that of gas.

Thus the refractive index increases as the absorption band is approached. A number of crystalline alkali halide has strong absorption bands in the ultraviolet. The nearer the band is to be the visible part of the spectrum, the more marked is the dispersion.

Abnormal dispersion occurs at resonant frequency, and at which the refractive index becomes to be smaller than unity (1.0) in much higher

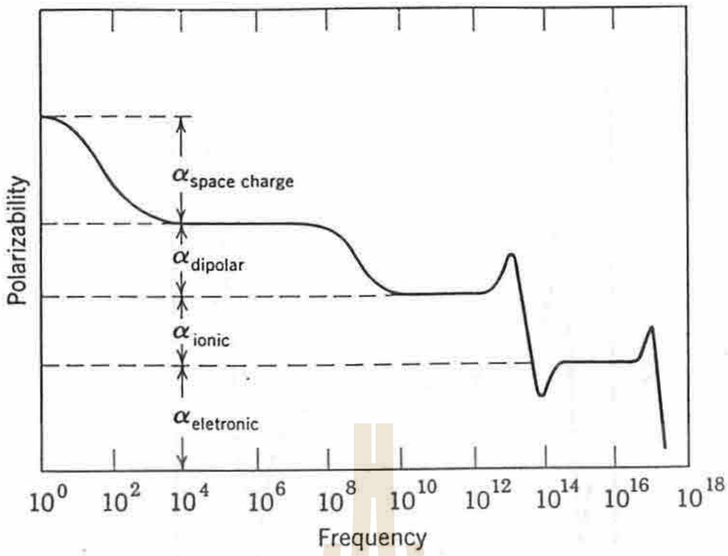


Fig. 18.5. Frequency dependence of several contributions to the polarizability (schematic).

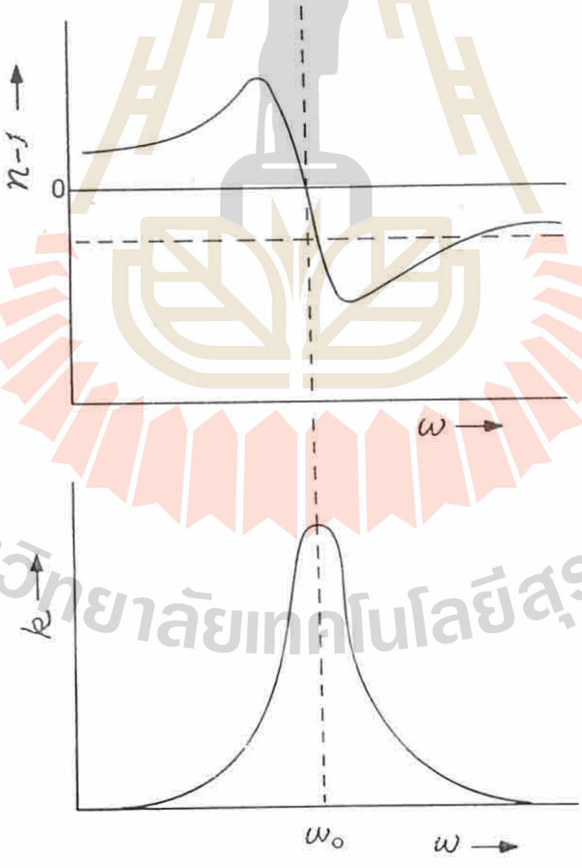


Fig. 94. Variation of $n-1$ and k with frequency (Lorentz theory).

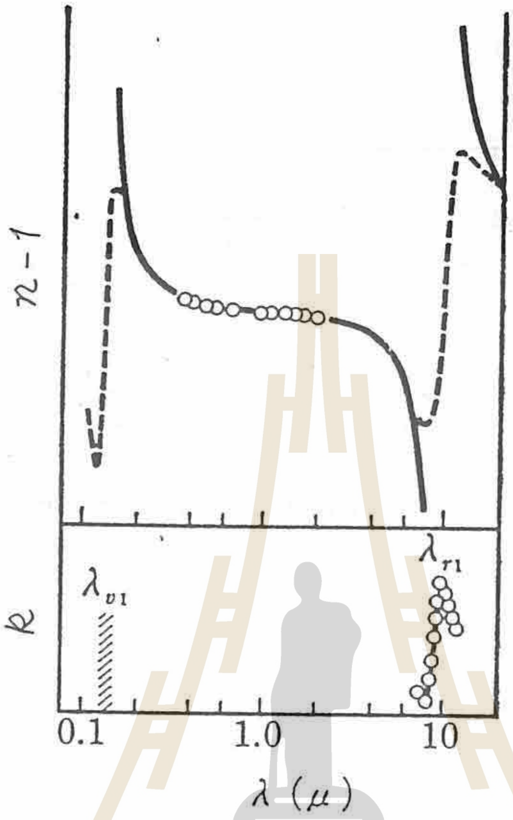


図 2.4　ガラスの吸収と分散

$$n-1=\frac{N_1e^2}{2\pi m}\sum\frac{f_i}{\nu_{0i}{}^2-\nu^2}$$

frequency region. On the contrary, the absorption coefficient k has small values except at resonant frequency.

In the region of the resonant frequency, the refractive index decreases with decreasing wavelength, and this is referred to as anomalous dispersion.

Normal Dispersion :

Refractive index decreases as the wavelength increases.

$\lambda \rightarrow$ longer $\qquad$ $n \rightarrow$ smaller

Abnormal Dispersion(Anomalous Dispersion) :

Refractive index decreases as the wavelength decreases.

$\lambda \rightarrow$ shorter $\qquad$ $n \rightarrow$ smaller

(3). Terminology of Dispersion

Dispersion values are quoted as differences between refractive indices at two specified wavelength.

- **Mean Dispersion**

  $\delta m = nF - nc,\ nd - nc,\ nd - nr,$ etc.
- **Partial Dispersion**

  $\delta I = (nx - ny)/(nF - nc)$ (x, y : various lines)
- **Relative Dispersion : Abbe Number**

  $\nu d = (nd - 1)/(nF - nc)$

The mean dispersion, (nF – nc) [F: 486.13nm, c: 656.27nm] covers the wavelength range between the hydrogen c and F lines. This amounts to most of the visible spectrum, including the important central region where the eye is most sensitive. The relative dispersion $\nu d=(nd-1)/(nF-nc)$ is called as ***Abbe Number***. It should be noted that the large Abbe number, the smaller dispersion.

(4). UV Absorption and Dispersion

The relationship between UV absorption and dispersion is very important for optical glasses. The mean dispersion, (nF – nc), increases with increasing basic oxide content of the glass. For both alkali silicate and borate glasses there is a shift of the UV transmission Cut-Off to longer wavelength as the alkali content increases. Thus for these systems at least, there is the expected correlation between UV absorption and dispersion.

Refractive index is related to the packing density of ions, the intensity of oscillator and absorption frequency, and the dispersion mainly can be determined by the absorption frequency. The dispersion would be

$$n_F\text{-}n_C = =(N_1 e^2/2\pi m)(\omega_F{}^2\text{-}\omega_C{}^2)\Sigma[f/(\omega_o{}^2\text{-}\omega_F{}^2)(\omega_o{}^2\text{-}\omega_C{}^2)]$$

$$\nu_d=(n_d\text{-}1)/(n_F\text{-}n_C)=[(\omega_o{}^2\text{-}\omega_F{}^2)(\omega_o{}^2\text{-}\omega_C{}^2)]/\ (\omega_F{}^2\text{-}\omega_C{}^2)(\omega_o{}^2\text{-}\omega_d^2)]$$

where N_1 is a number of oxygen ions per unit volume, e and m are the charge and mass of electron respectively, ω_o is the characteristic absorption frequency of oxygen, f is the intensity of oscillator, and ω is the frequency of light. From these equations, one can conclude that the refractive index is the function of packing density and intensity of oscillator, and a mean dispersion can be determined mainly by the wavelength of absorption peak. And the Abbe nuber is the function of the wavelength of absorption peak approximately. The dispersion is expected to be large with the longer wavelength of the absorption peak. Also the Abbe number increases with increase in ω_o(shorter λ_o).

The mean dispersion, (nF – nc), increases with increasing basic oxide content of the glass. For both alkali silicate and borate glasses there is a shift of the UV transmission Cut-Off to longer wavelength as the alkali content increases.

Pb^{2+}, Ti^{4+}, Nb^{5+}, Ba^{2+}, La^{3+}, Y^{3+}, Th^{4+}, Ta^{5+} ions provide a higher refractive index of glass. By the measurements of the absorption spectrum in UV region, it is found that Pb^{2+}, Ti^{4+}, Nb^{5+} ions give high dispersion glass having the absorption of longer wavelength in UV region, Ba^{2+}, La^{3+}, Y^{3+}, Th^{4+}, Ta^{5+} ions provide low dispersion having the absorption of shorter wavelength. Finally, one can classify the components to higher refractive index-higher dispersion(TiO_2, PbO, etc.), higher refractive index-lower dispersion(La_2O_3, Gd_2O_3, Y_2O_3, ZrO_2, Ta_2O_5, etc.), and lower refractive index-lower dispersion(P_2O_5, Fluoride, etc.).

In optical glasses, the dispersion can be expressed by

$$n^2\text{-}1=KN_1f_1/(1/\lambda_1{}^2\text{-}1/\lambda^2)+KN_2f_2/(1/\lambda_2{}^2\text{-}1/\lambda^2)+KN_3f_3(1/\lambda_3{}^2\text{-}1/\lambda^2)$$
$$KN_4f_4/(1/\lambda_4{}^2\text{-}1/\lambda^2)$$

where first term is caused by the absorption of bridging oxygen ions, the second term is the absorption of non-bridging oxygen ions, the third term the absorption of cations(e.g. Pb^{2+}) and fourth term the absorption in IR region. From this equation, one can consider the reason of the changes in dispersion of optical glass.

(5). Abnormal Dispersion

A group of glasses exhibits different features at the shorter and longer wavelength in the relationship between the refractive index and

- Abnormal partial dispersion glass
- Most poor water and acid durability in optical glass

(12). ZnK
- SiO_2-R_2O-ZnO system
- Low refractive index and low dispersion
- Good water durability
- Low thermal expansion

Recently, new glass system has been developed.

①. High refractive index and low dispersion glass

Although it is clear that CdO and ThO_2 provides the wider glass forming region and avoiding devitrification, their use is prohibited by environmental problem(CdO:toxicity, ThO_2:radioactivity). (Gd_2O_3+Y_2O_3) were used instead of ThO_2 and (BaO+Nb_2O_5) were used instead of CdO.

②. High dispersion glass

Glasses containing high-PbO has been used as high dispersion glass, their hardness was low of 365Kg/mm^2 in Knoop hardness. New glass system of SiO_2-TiO_2-Nb_2O_5-RO-Li_2O was developed. This glass system is low density and high hardness and exhibits good chemical durability. Their Knoop hardness is 550Kg/mm^2. However, the coloration is greater than PbO-containing glasses, and the stability for devitrification is not high enough.

③. Low dispersion glass

The glass system of P_2O_5-AlF_3-RF_2-RF has been developed. For example, FCD 10 has n_d:1.45650 and ν_d : 90.8, large Abbe number with extremely low dispersion. And this glass exhibits a large abnormal partial dispersion in a blue portion of visible region. It is quite valuable for apochromatic telephoto-lens.

④. Low density and high refractive index glass

BaFD15 glass is a borosilicate system containing Li_2O, TiO_2 and Nb_2O_5. Its n_d is 1.70 and ρ is 2.99, and useful for ophtalmic lens.

The composition and some properties of optical glasses are shown in next page.

(2). Composition Design of Optical Glasses

As already mentioned in previous chapter(Refractive index and dispersion), the refractive index can be determined by increasing in an ionic refractivity of oxygen ions and packing density of oxygen ions.

On the other hand, the dispersion can be decided by the absorption in UV and IR regions, especially in UV region. A larger absorption near visible region provides larger dispersion.

- Ta_2O_5, Y_2O_3, Gd_2O_3, La_2O_3 containing glass
- $ThO_2 \rightarrow Gd_2O_3, Y_2O_3$
- TaSF: Highest refractive index and low dispersion in n_d-ν_d diagram, n_d : over 1.85
- Excellent water durability, high hardness
- TaF, TaK: $Ta_2O_5 \rightarrow Gd_2O_3, Y_2O_3$, $B_2O_3 \rightarrow$ increase

(6). PSK-PK and BK

- SiO_2-B_2O_3-R_2O-RO system
- No P_2O_5
- PK>BK: B_2O_3
- PSK>PK: BaO
- Lowest refractive index and low dispersion
- BK7 : most famous optical glass

(7). PSKS-PKS

- P_2O_5-R_2O-RO system
- Al_2O_3 and B_2O_3 are added to improve chemical durability
- Low refractive index and low dispersion
- Very poor water durability

(8). FK

- SiO_2-B_2O_3-K_2O-KF system
- Small amount of Al_2O_3 to prevent devitrification
- Low refractive index and low dispersion
- Poor acid resistivity
- Volatile of fluoride

(9). TiSF-TiF-TiK

- SiO_2-TiO_2-KF system
- Low refractive index and high dispersion
  low n_d: fluoride, high dispersion: TiO_2
- Tend to make striae by the volatilization of fluoride

(10). KzF

- SiO_2-B_2O_3-R_2O-Sb_2O_3 system
- $PbO \rightarrow Sb_2O_3$ in (1) glass system
- Small partial dispersion in blue portion of visible region
  $PbO \rightarrow Sb_2O_3$
- Large partial dispersion in red portion of visible region
  B_2O_3
- Abnormal(anomalous) partial dispersion glass
- Very poor water durability

(11). KzFS

- B_2O_3-PbO system

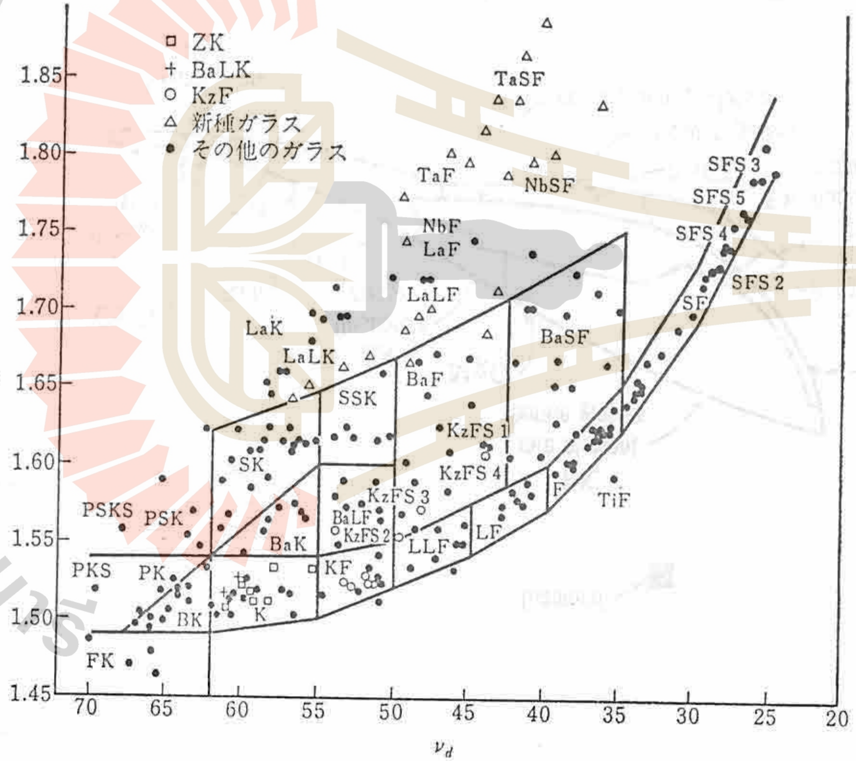


図 2.1　光学ガラス一覧表（保谷硝子カタログ）

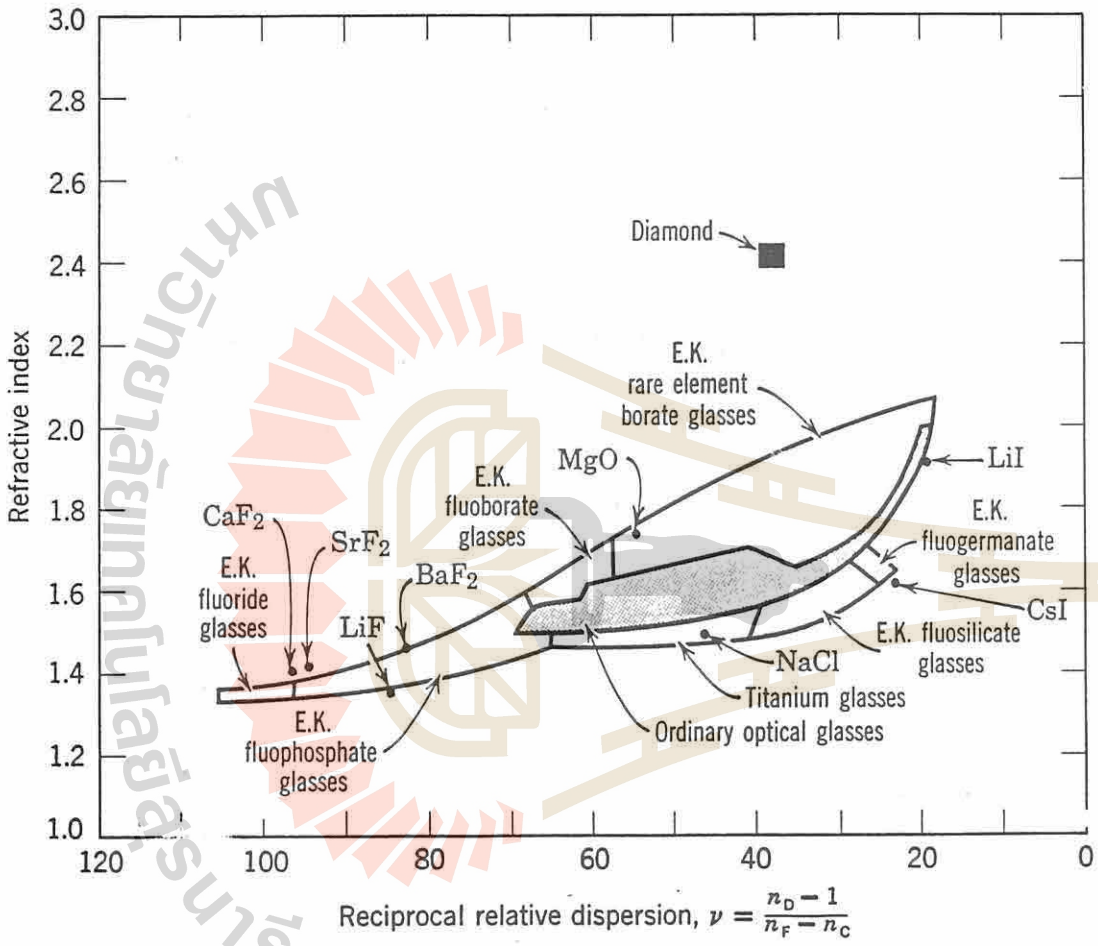


Fig. 13.10. Range of optical properties obtained with crystals and ordinary optical glasses and with Eastman Kodak Company fluoride and rare earth glasses.

(2). BaSF-BaF-BaLF and BaK-BaLK

- SiO_2-PbO-BaO-R_2O system
- BaO containing glass instead of PbO
- BaK, BaLK: SiO_2-BaO-R_2O system
- Higher refractive index, smaller dispersion than PbO containing glasses
- Abbe Number is not so small.

(2)'. BaSF-BaF-SSK-SK

- Non-Alkakli, SiO_2-B_2O_3-PbO-BaO system
- SSK, SK: Non-PbO SiO_2-B_2O_3-BaO system
  High refractive index and low dispersion
- SK16, SK18, SSK5, BaF10, BaSF7, BaSF8:
  Highest refractive index in silicate glass system, containing TiO_2, improved chemical durability

(3). LaF-LaK

- This glass system has been developed by Eastman-Kodak after World War II. New glass system
- (SiO_2)-B_2O_3-La_2O_3-PbO-Al_2O_3, (SiO_2)-B_2O_3-La_2O_3-PbO-RO, (SiO_2)-B_2O_3-La_2O_3-ZrO_2-RO glass systems.
- La_2O_3 containing borate glass
- LaK: RO→ZnO, CaO, SrO, BaO
- LaF: PbO, TiO_2 containing
- High refractive index.
- Acid resistivity is poor.
- Small amount of SiO_2 and ZrO_2 are added to prevent devitrification

(3)' LaLF-LaLK

- B_2O_3-La_2O_3-RO system
- La_2O_3 →RO
- Most poor chemical durability similar to KzFS

(4). NbSF - NbF

- B_2O_3-La_2O_3-RO-Nb_2O_5 system
- CdO→ZnO
- Addition of Nb_2O_5 instead of La_2O_3
- Small amount of SiO_2 and ZrO_2 are added to prevent devitrification
- NbSF: TiO_2, WO_3 containing
- High refractive index
- Fairly good acid and water durability

(5). TaSF-TaF-TaK

- B_2O_3-La_2O_3-ThO_2(Gd_2O_3,Y_2O_3)-(Ta_2O_5-Nb_2O_5) system

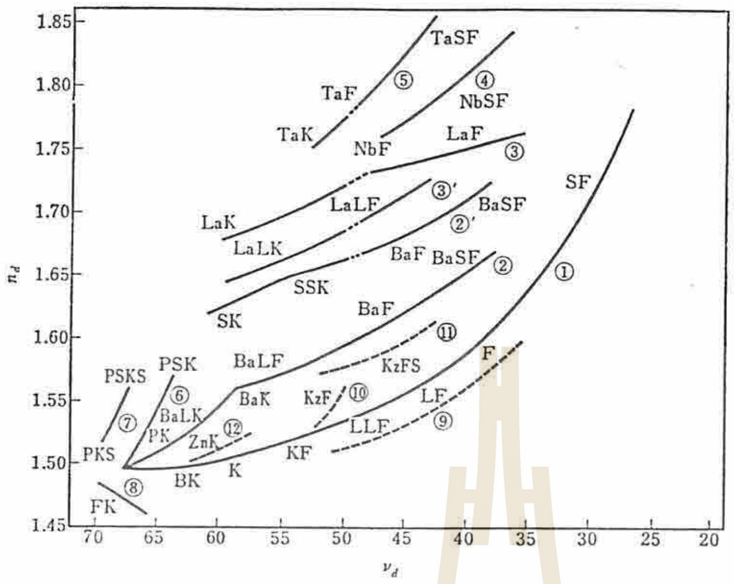


図 2.2 光学ガラスの分類系列

表 2.2 光学ガラスの組成

	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			
BaSF2	23.6	10.5	1.5			7.0	5.9	29.3	14.2	0.4	0.6		7.0	
BaF10	30.9	9.2	0.3			4.0	5.3	41.3	4.6		0.3		3.6	
BaLF1	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			0.6			
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			
SK1 6	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			
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

1. Terminology of Optical Glass

The optical glasses are usually called some symbols, such as SK, F, etc. These symbols are as follows:

K : Kronglas(Crwon Glass) : $\nu > 55$
F : Flintglas(Flint Glass) : $\nu < 50$

And a prefix and/or suffix are also as follows:

S : Schwer (Dense)
SS: Schwerst(Extra Dense)
L : Leicht(Light)
LL: Doppel-Leicht(Extra Light)

2. Classification of Optical Glass-Composition and Properties

The refractive index n_d and Abbe number(dispersion) ν can be used for classification of optical glass, and there are two main category of optical glass, i.e. crown glass and flint glass. Crown glass has ν of over 55 and flint glass has ν of below 50.

Though an over 200 of optical glasses has been listed in optical glass catalogue, they can be classified into 12 kind of glass systems based on the character of composition.

(1). Classification of Optical Glasses

(1). SF-F-LF-KF and K: Classical glass system

- $SiO_2 - PbO - R_2O(K_2O)$ glass system.
- SF→F→LF→LLF→KF→K : $PbO\downarrow$, $SiO_2\uparrow$, $R_2O\uparrow$
  n_d→decrease, ν_d→increase(dispersion→decrease)
  K: BaO and CaO instead of PbO
- SF : 70% PbO, Pale yellow, small Abbe Number (ν_d)
- SFS extra dense flint(TiO_2 containing): large partial dispersion

表 2.1 光学ガラスの主要成分

	Flint	Kron
1	SiO_2-PbO-R_2O	$\longrightarrow$ SiO_2-RO-R_2O
2	SiO_2-PbO-BaO-R_2O	$\longrightarrow$ SiO_2-BaO-R_2O
2′	SiO_2-B_2O_3-PbO-BaO	$\longrightarrow$ SiO_2-B_2O_3-BaO
3	(SiO_2)-B_2O_3-La_2O_3-PbO-Al_2O_3	$\longrightarrow$ (SiO_2)-B_2O_3-La_2O_3-RO-ZrO_2
3′	(SiO_2)-B_2O_3-La_2O_3-PbO-RO	$\longrightarrow$ (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	$\longrightarrow$ (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	$\longrightarrow$ 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

X. Optical Glasses

The homogeneity is the most significant requirement for optical glasses. The technical efforts are focused only on the homogeneization of glass. The stirring, fine annealing and using platinum vessel can be applied for this purpose in optical glass industry. The properties required for optical glasses are:

(1). Transparent and colorless
(2). Optically homogeneous and isotropic
(3). Bubbles, striae, cord and strain free
(4). Specified optical constant(refractive index and dispersion)
     small dependence of temperature
(5). Good mechanical properties(hardness, elasticity)
(6). Good chemical durability

One of the characteristic points of optical glass is that there are so many kind of glass. Camera lenses consist of more than four single lenses, especially in zoom lenses consist of over 10 single lenses. Thus, so many optical glasses are necessary in order to eliminate chromatic, and Seidel's 5 aberrations. On account of the elimination of these aberrations more than two lenses having different refractive index should be combined.

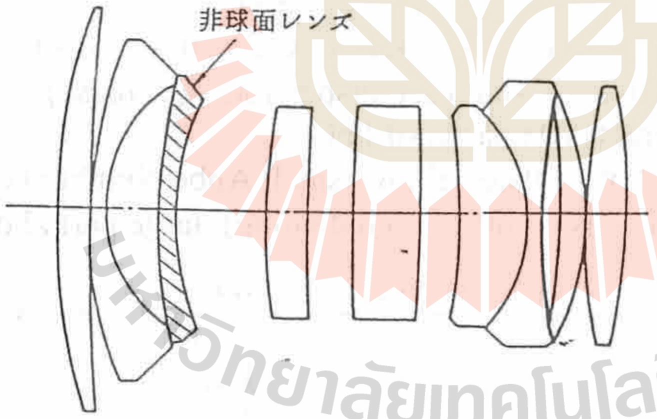


図 17　シグマ f ＝28mm，F 1.8 のレンズ構成

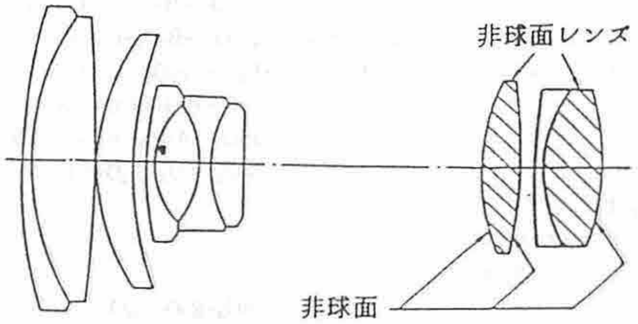
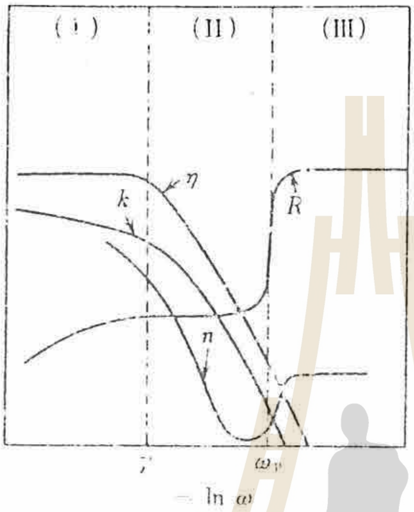


図 15　松下ビデオカメラ NV−S5 のレンズ構成

Normally the density of conduction electron is very high in metals, the plasma frequency lies in UV region. And the relaxation frequency is the order of $10^{13}s^{-1}$, i.e. in IR region. Therefore, the visible light is reflected, UV light can transmit.



On the contrary, in the case of dielectrics or semiconductors the electron density is lower than that of metals, therefore the plasma angular frequency would be lower, these materials should be transparent in practical frequency region of light. Since the band gap of semiconductors is small, the visible light can be absorbed.

For example, in the case of SnO_2. Its band gap is about 3.6eV(344nm). So that this material is transparent in visible region.

$\mu \approx 2.40\text{x}10^{-2}m^2 \cdot V^{-1} \cdot s^{-1}$

$m^* \cong 0.40m_o(m_o\text{=}9.0\text{x}10^{-31}Kg)$

$e = 1.60\text{x}10^{-19}C$

$\gamma = 1.85\text{x}10^{13}s^{-1}$

Plasma resonance takes places at above $n\sim 7.8\text{x}10^{22}m^{-3}(7.8\text{x}10^{16}cm^{-3})$.
Now one can estimate $n\text{=}10^{17}cm^{-3}$, the plasma frequency $\omega p\text{=}2.1\text{x}10^{13}s^{-1}$. This corresponds to about 2.3μm, and the light having longer than 2.3μm can be reflected. The shorter wavelength of light of 2.3 μm can transmit.

would be larger, the second term decreases markedly. In this case, a slight amount of light energy goes into the metal and spends as a Joule heat.

In metals or semiconductors the conductive electron interacts with light, n and k correlate strongly to the mean free path, mobility and effective mass of conductive electrons. When the light incidents to the material having conductive electron, electrons absorb the energy of E=hν. In the wavelength of light is longer than the mean free path of electrons, electrons collide with lattice few times during the light progresses by one wavelength, electrons provide the energy to the lattice. Since this energy spends as a heat energy, the light can be absorbed. This absorption is called a conduction absorption.

When the wavelength of light is shorter enough than the mean free path of electrons, electrons plays as a free electron and gives back the energy which is absorbed once. Hence the absorption does not occur. Actually, electrons play a free electron as the frequency of light is higher than the specified frequency. This frequency is called plasma frequency. Above the plasma angular frequency, electrons do the plasma vibration with the change of charge density, thus the light can transmit.

By he simplification of above equation, $(n^2 - k^2)$ and nk are given by

$$(n^2 - k^2) = (\omega^2 - \omega_p^2)/(\omega^2 + \gamma^2)$$

$$2nk = \gamma(\omega_p^2 + \gamma^2)/\omega(\omega^2 + \gamma^2)$$

$\gamma = e/m^*\mu$: relaxation frequency

$\omega_p^2 = (ne^2/\varepsilon_o m^*) - \gamma^2$: plasma frequency

e: electron charge

n: density of conductive electron

m*: effective mass of electron

μ: mobility

ε_o: dielectric constant in vacuum

γ: relaxation frequency(reciprocal of relaxation time of electron

where the relaxation frequency indicates the number of collision with the lattice per unit time.

① $\omega \ll \gamma$ $R = 1 - 2n\,(2\omega\varepsilon_o/\sigma)^{1/2}$ Reflection/absorption by conduction

② $\gamma < \omega < \omega_p$ $R = 1 - 2n\,(2\omega\varepsilon_o/\sigma)^{1/2}$ Reflection

③ $\omega_p \ll \omega$ $R = 0$ Transmission

$$2nk = (\sigma_o/\omega\varepsilon_o)[1/(1+\omega^2/g^2)]$$
$$+\Sigma[(N_k e^2/m\varepsilon_o)(\omega_k^{\ 2} - \omega^2)]/[(\omega_k^{\ 2} - \omega^2)^2 + \omega^2 g_k^{\ 2})]$$

As ω becomes smaller than σ/ε_o, the first term of nk is larger than unity. And one can recognize that the effect of restrained electron decreases markedly concealing by the effect of conduction electrons at lower frequency. On the other hand, $(n^2 - k^2)$ is not so large, and becomes a finite value at the limit lowering the frequency. The nk becomes larger with decreasing ω, therefore n must be equal to k at that limit. From above

$$n^2 \approx k^2 \approx = \sigma_o/2\omega\varepsilon_o$$

and finally

$$n \approx k \approx (\sigma_o/2\omega\varepsilon_o)^{1/2}$$

As the frequency of electro-magnetic wave approaches from IR to visible region, ω would be the order of ω_k, the absorption caused by restrained electron can not be negligible. The effect of conduction electron is complicated. Therefore, the relation between $(n^2 - k^2)$ and nk, and ω exhibits very complicated features.

In the UV region, the dispersion caused by restrained electron increases because of decreasing of the effect of conduction electrons.

Now consider the reflection of the media such as metals, which absorbs the light energy. The refractive index can be expressed as the complex, n−ik,

$$Ex''/Ex = [n-(n'- ik')]/[n+(n'-ik)]= [(n-n')+ik']/[(n+n')-ik]$$

The refractivity can be given by the square of above Eq.

$$R=[(n-n')^2+k'^2]/[(n+n')^2-k^2]$$

At relatively low frequency, both n' and k' are almost same as $(\sigma/2\omega\varepsilon_o)^{1/2}$, which is greater than n or unity. Therefore,

$$R = 1- 2n\ (2\omega\varepsilon_o\ /\sigma)^{1/2}$$

The second term is small(σ_o is large), the R approaches to unity, that is, almost all incident light can reflect. Further, as ω would be small or σ

Dispersion of light in Metals

The metal involves electrons which moves freely in the ion lattice, and its can transport the electric current. Only the electrical field E can be applied to electrons, and it is eE. It is considered that a restoring force may be zero in the equation of the motion, i.e. ω_o is zero:

$$M(d^2X/dt^2) + mg(dX/dt) + m\omega_o{}^2X = eE$$
$$[M(d^2X/dt^2) + mg(dX/dt) = eE]$$

Here, assuming the damping force can be applied proportional to their velocity. The current density J may be given by

$$J=Nev=Ne^2E/mg=\sigma E, \quad \sigma = Ne^2/mg$$

$E=E_oe^{(i\omega t)}$, then the conductivity σ is given by

$$\sigma = Ne^2/(mg+im\omega)$$

The electrical conductivity changes with frequency of electro-magnetic wave, it becomes to zero as the frequency approaching to infinite.

Now considering propagation of electo-magnetic wave, the dielectric constant can be given by

$$\varepsilon = (n - ik)^2 = ke - i\sigma/\omega\varepsilon_o$$

ke is given by

$$ke = 1 + \Sigma[N_ke^2/m\varepsilon_o]/[\omega_k{}^2 - \omega^2 + i\omega g_k]$$

$$-i\sigma/\omega\varepsilon o = -iNe^2/[(mg + mi\omega)\omega\varepsilon_o] = iNe^2/(-\omega^2 + i\omega g)$$

Therefore,

$$(n\text{-}ik)^2 = 1 - iNe^2/(-\omega^2 + i\omega g) + \Sigma(N_ke^2/m\varepsilon_o)/(\omega_k{}^2 - \omega^2 + i\omega g_k)$$

$$n^2 - k^2 = 1-(\sigma_o/g\varepsilon_o)[1/(1+\omega^2/g^2)]$$
$$+\Sigma[(N_ke^2/m\varepsilon_o)(\omega_k{}^2 - \omega^2)]/[(\omega_k{}^2 - \omega^2)^2 + \omega^2g_k{}^2)]$$

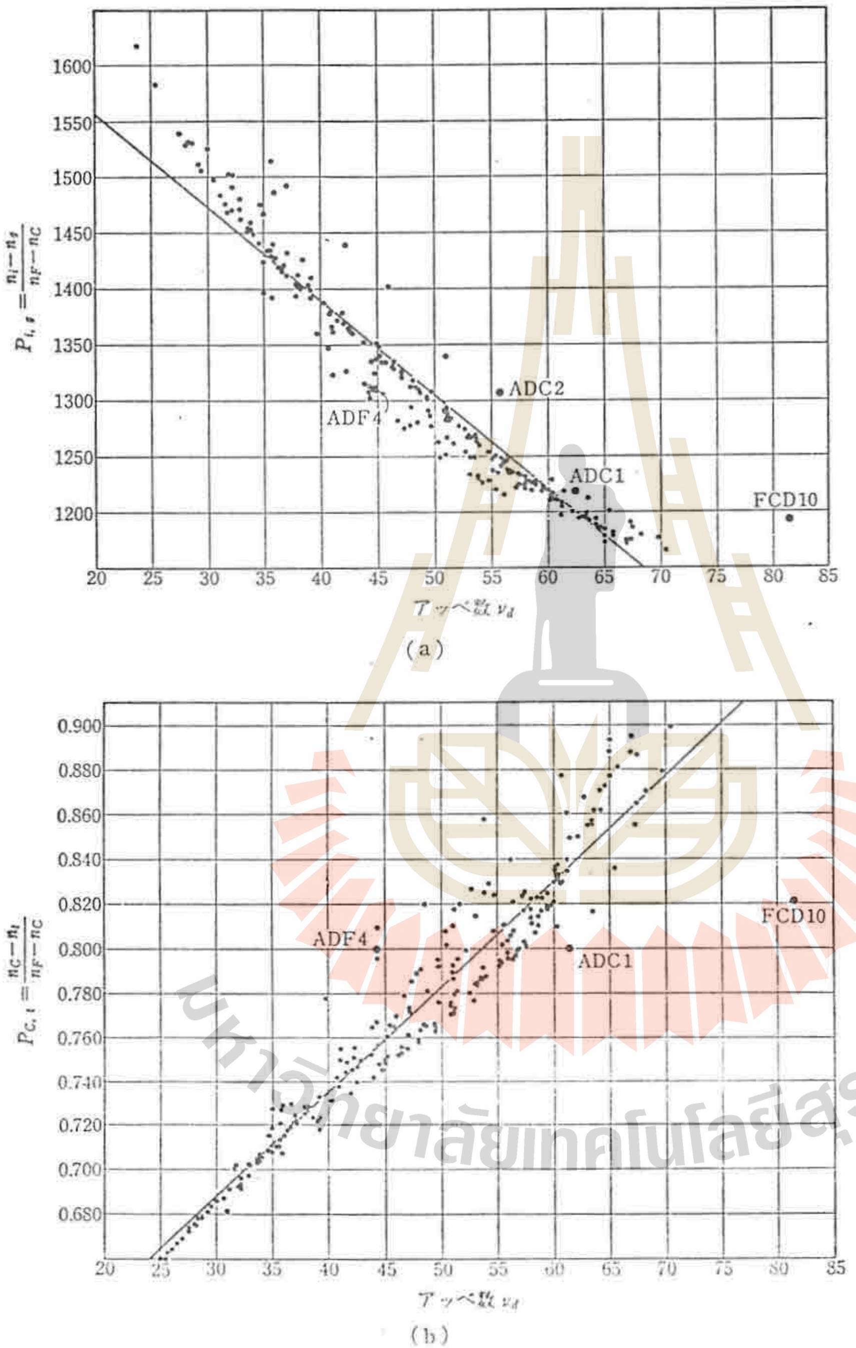
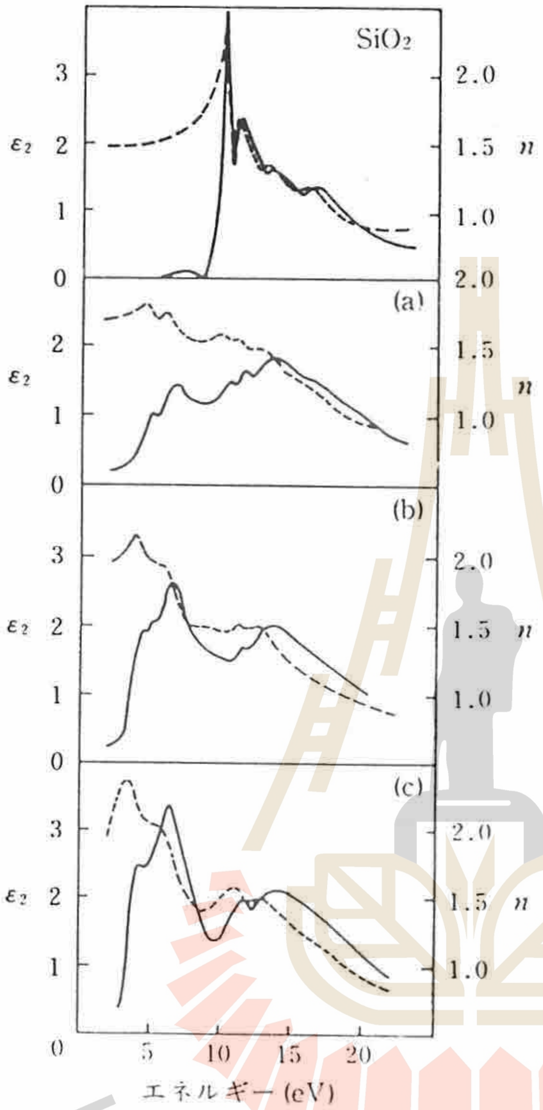


図 5.3　部分分散とアッベ数の関係　（a）短波長　（b）長波長



（ａ） 29.3PbO・5.8K_2O・64.8 SiO_2,

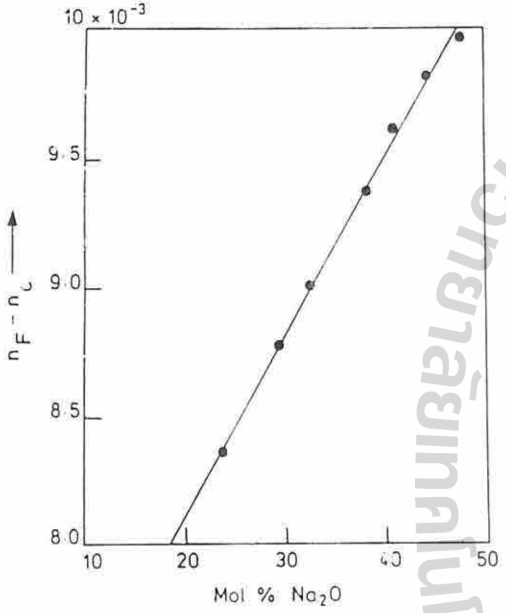
（ｂ） 57.8 Pb(

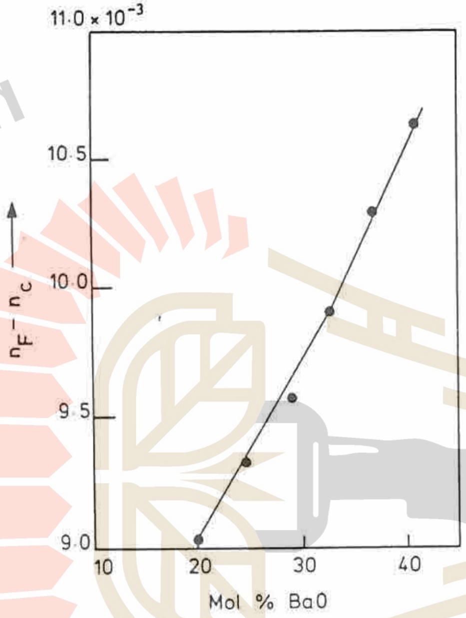
（ｃ） 91.2 PbO・8.8 SiO_2

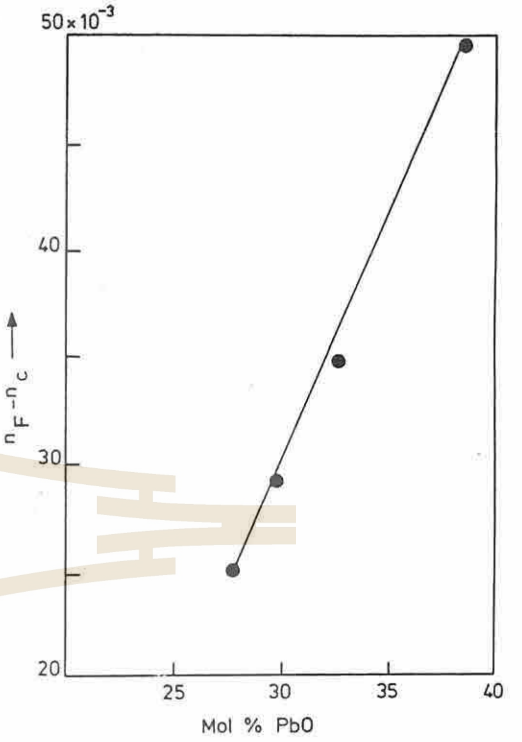
図－3　PbO 含有ガラスの屈折率 n (点線)と吸収 ε_2'' (実線)

(反射スペクトルのクラマース・クって得た)

〔E. Ellis, D. W. Johnson, A. Breeze, P. M. Mans : *Phil. May.*, B40, 125(1979).〕


10 × 10^{-3}
9.5
9.0
8.5
8.0
$n_F - n_c$ →
10
20
30
40
50
Mol % Na_2O


11.0 × 10^{-3}
10.5
10.0
9.5
9.0
$n_F - n_c$ →
10
20
30
40
Mol % BaO


50 × 10^{-3}
40
30
20
$n_F - n_c$ →
25
30
35
40
Mol % PbO

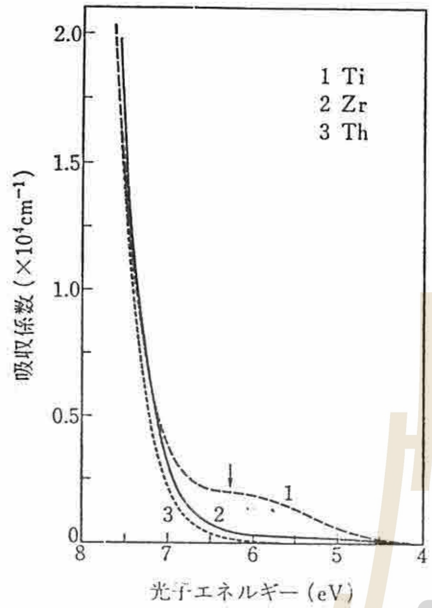


図 2.23　10.8BaO-0.2$R_{m/n}$O-89$B_{2/3}$O
ガラスの吸収スペクトル（1）

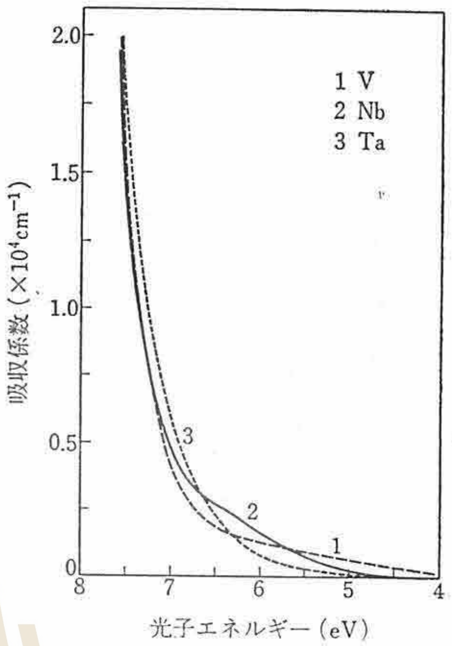


図 2.24　10.8BaO-0.2$R_{m/n}$O-89$B_{2/3}$O
ガラスの吸収スペクトル（2）

あった．Va 族でも，Nb を含むガラスの吸収が 6.8 eV（182 nm）にピークをもつことが見いだされた（図 2.24）．この吸収は還元雰囲気で溶解された場合も

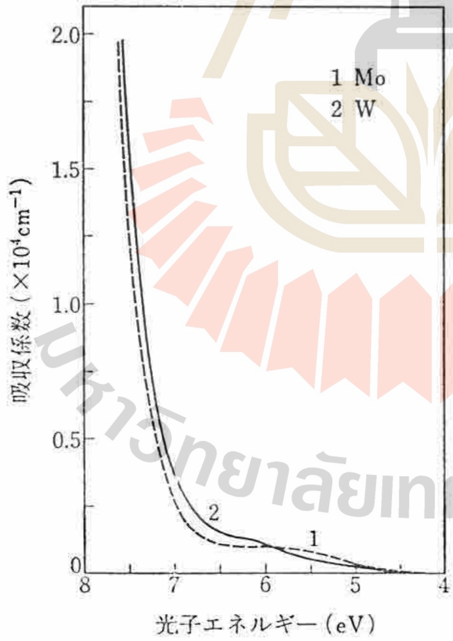


図 2.25　10.8BaO-0.2$R_{m/n}$O-89$B_{2/3}$O
ガラスの吸収スペクトル（3）

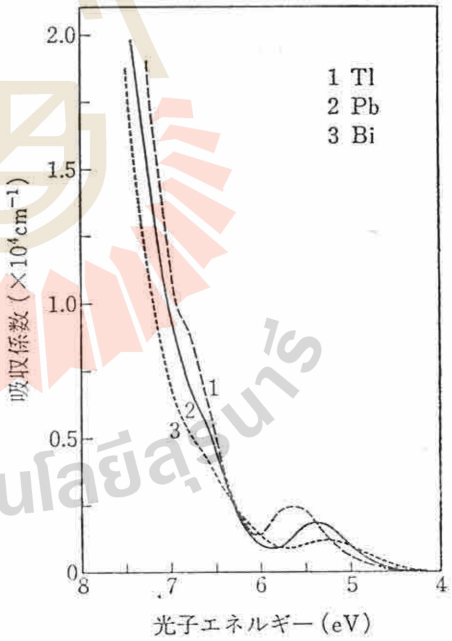


図 2.26　10.8BaO-0.2$R_{m/n}$O-89$B_{2/3}$O
ガラスの吸収スペクトル（4）

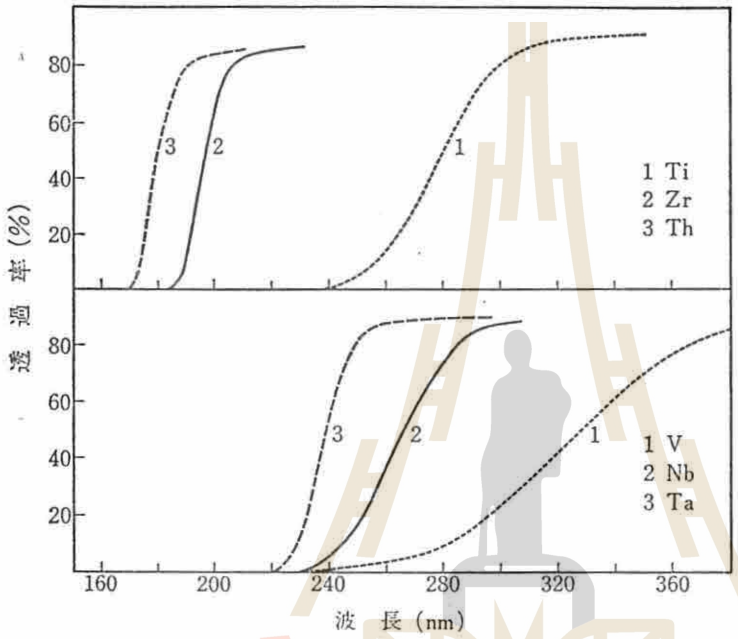


図 2.21　$10BaO\text{-}5R_{m/n}O\text{-}85B_{2/3}O$ ガラスの透過スペクトル（2）

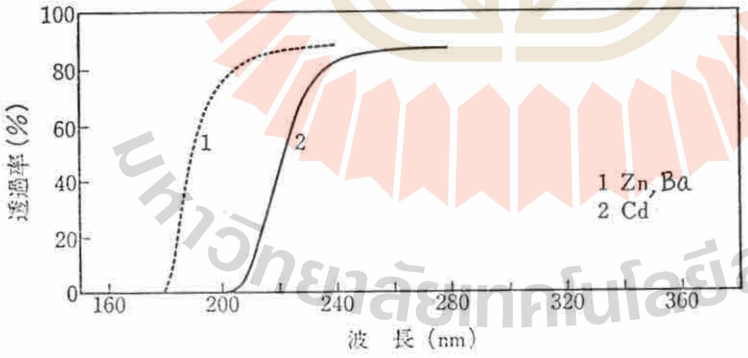
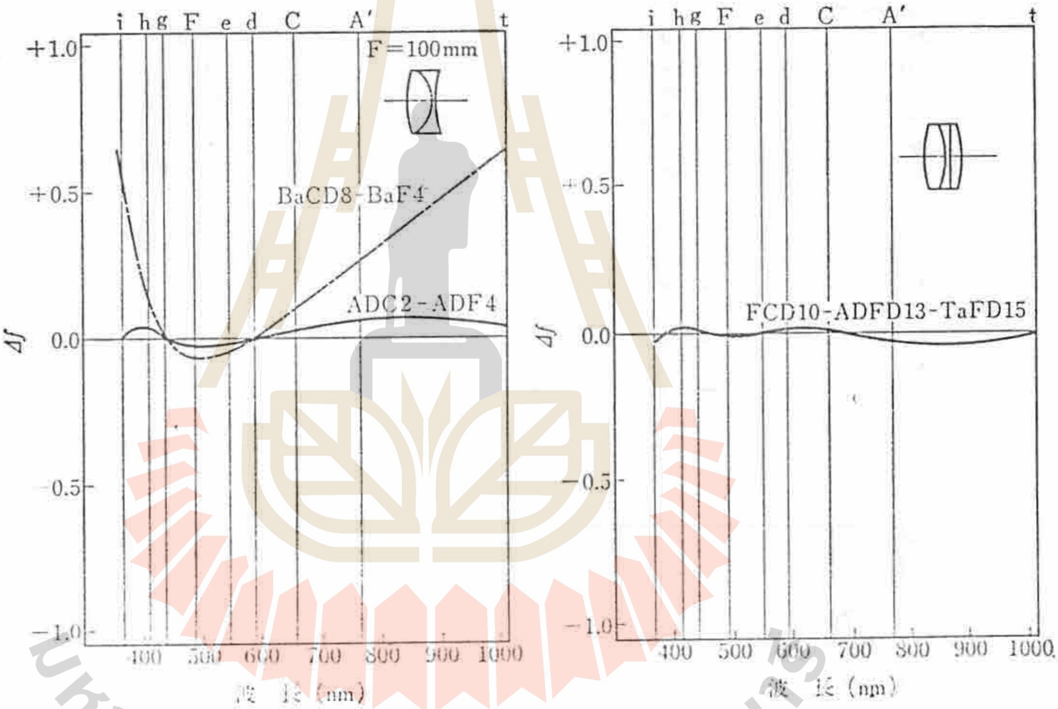


図 2.22　$10BaO\text{-}5R_{m/n}O\text{-}85B_{2/3}O$ ガラスの透過スペクトル（3）

表 5.3 通常のガラスと比較した異常部分分散ガラスの特性

	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	$P_{F,g}$	$P_{C,t}$
ADC 1	.0634	225.13	.127	40.85	.155	.790	—	—	10.0	.00793	1.62000	62.19	1.2268	.7955
BK 6	.0684	166.29	.108 .124 .141	18.20 14.09 4.52	.175	.509	—	—	9.7	.00934	1.53113	62.15	1.2019	.8500
ADC 2	.0634	228.32	.127 .139	32.10 1.00	.155	.660	.234	.687	10.0	.01013	1.59700	55.29	1.3126	.8022
K 10	.0684	143.09	.106 .122	18.83 18.00	.172	2.095	.196 .237	.140 .088	9.8	.00832	1.50137	56.41	1.2463	.8213
ADF 4	.0684	201.07	.111 .139	3.01 20.02	.172	3.188	.180 .238	1.899 .468	7.7	.01298	1.61250	44.87	1.3237	.8002
LLF 4	.0684	150.70	.106 .122	18.71 17.50	.175	5.883	.199 .242	.389 .304	9.8	.00836	1.56138	45.23	1.3398	.7608

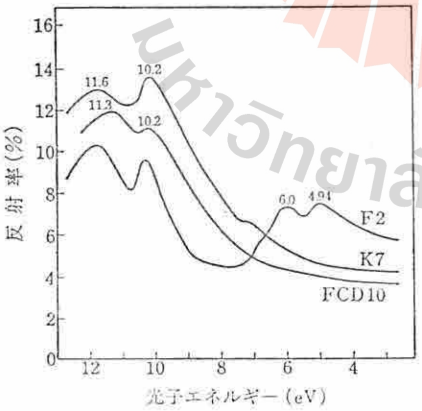


(a)　　(b)

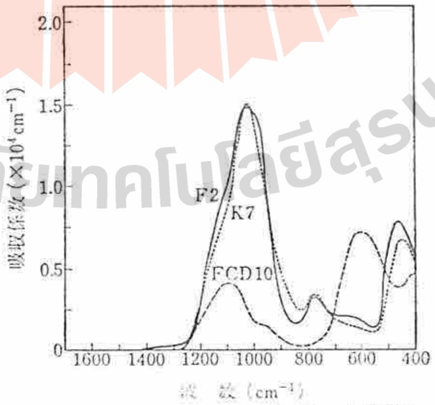
図 5.4 色消しレンズの色収差特性の一例 (a) ADC2-ADF4 (b) FCD10-ADF8-TaFD15

表 5.2　紫外および赤外固有吸収の波長と強度（計算による）

	FCD 10	K 7	F 2
n_d	1.45650	1.51112	1.62004
ν_d	90.77	60.41	36.37
$P_{i,g}$	1.1725	1.2179	1.4194
$P_{C,t}$	.8357	.8315	.7175
λ_0 (μ)	.0679	.0684	.0684
KN_0f_0	189.13	151.40	158.62
λ_1 (μ)	.110　.122	.106　.122	.106　.122
KN_1f_1	18.02　.85	19.10　18.27	17.38　14.89
λ_2 (μ)	—	.172	.181
KN_2f_2	—	1.93	9.94
λ_3 (μ)	—	—	.207　.251
KN_3f_3	—	—	1.04　.40
λ_4 (μ)	12.0	9.8	9.8
KN_4f_4	.00453	.00825	.00840
calc-meas			
Δn_t	−.00000	−.00000	.00000
Δn_s	−.00001	−.00000	−.00000
Δn_r	−.00001	−.00000	−.00000
Δn_C	−.00000	−.00000	−.00000
$\Delta n_{C'}$	−.00000	−.00000	−.00000
Δn_D	.00000	−.00000	−.00000
Δn_d	.00000	−.00000	−.00000
Δn_e	.00000	−.00000	−.00000
Δn_F	−.00000	−.00000	−.00000
$\Delta n_{F'}$	−.00000	−.00000	−.00000
Δn_g	−.00001	−.00000	.00000
Δn_h	−.00001	.00000	.00001
Δn_i	−.00001	−.00000	−.00000



（a） FAD10, K7 および F2 の反射スペクトル（真空紫外～可視域）



（b） FCD10, K7 および F2 の赤外吸収スペクトル

wavelength. In normal optical glasses, an approximate linear relationship between the partial dispersion and Abbe number can be observed both in shorter and longer wavelength regions: $P_{i,g}=(n_i-n_g)/(n_F-n_C)$, $P_{C,t}=(n_C-n_t)/(n_F-n_C)$. Glasses deviated from these linear relations are called an ***abnormal partial dispersion glass***. It is well known that these abnormal partial dispersion glasses are quite effective to eliminate the chromatic aberration.

Here, we can consider the reason of the abnormal partial dispersion of various optical glasses. For example, FCD10, ADC1, ADC2 and ADF4 are the typical glasses which exhibit abnormal dispersion.

①. FCD10(Fluoro-phosphate glass)

In this glass, the UV absorption peak caused by $(AlF_6)^{3-}$ lies at 110nm which shorter than that of bridging oxygen ions(106 and 120nm), and its absorption intensity is small. And there is no absorption caused by non-bridging oxygen ions. Further, the absorption intensity caused by P_2O_5 in IR region is small. As a result, the abnormal dispersion of FCD10 glass can be explained by the UV absorption being shorter wavelength and weak IR absorption.

②. ADC1, 2(Phosphate glass)

ADC1 has a strong UV absorption and weak IR absorption. These provide the abnormal dispersion to ADC1 glass. ADC2 has a strong absorption in UV region caused by P_2O_5 and Ti^{4+}, and weak absorption in IR region. The reason of a large Abbe number of ADC glasses is caused by the absorption of non-bridging oxygen ions being shorter wavelength.

③. ADF4(Kurz-flint glass)

This glass is borate glass system containing PbO. This glass has a strong IR absorption caused by B_2O_3 and weak absorption in UV region.

By using these abnormal dispersion glasses for the apochromatic lens, the aberration becomes quite small.

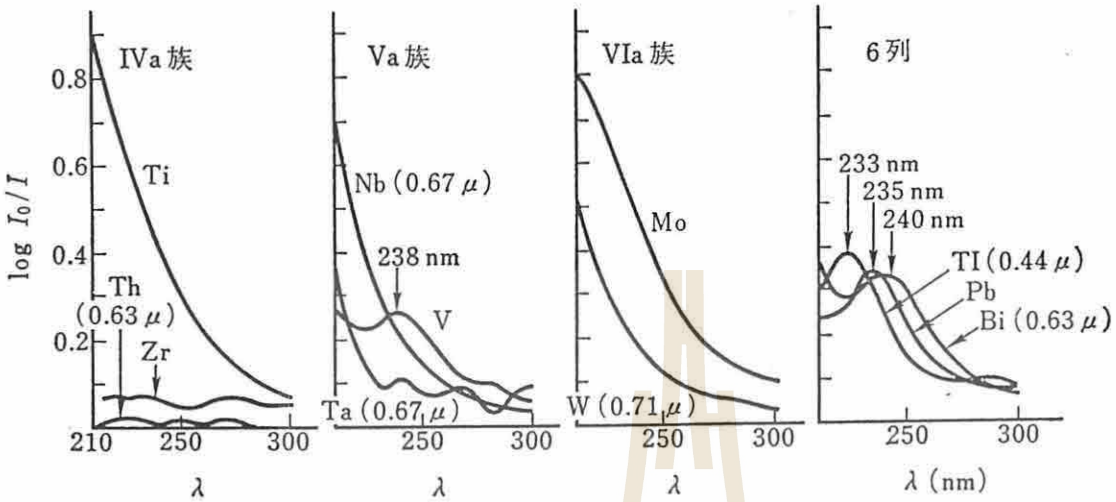


図 2.5 紫外光域における BO$_{1.5}$ 80, BaO18, MOn2 ガラスの吸収

$$n_d - 1 = \frac{N_1 e^2}{2\pi m} \sum \frac{f}{\nu_0{}^2 - \nu_d{}^2}$$

$$n_F - n_C = \frac{N_1 e^2}{2\pi m} (\nu_F{}^2 - \nu_C{}^2) \sum \frac{f}{(\nu_0{}^2 - \nu_F{}^2)(\nu_0{}^2 - \nu_C{}^2)}$$

$$\nu_d = \frac{n_d - 1}{n_F - n_C} = \frac{(\nu_0{}^2 - \nu_F{}^2)(\nu_0{}^2 - \nu_C{}^2)}{(\nu_F{}^2 - \nu_C{}^2)(\nu_0{}^2 - \nu_d{}^2)}$$

Dispersion : determined by the wavelength of absorption peak
longer wavelength→large dispersion
Abbe Number: determined by the wavelength of absorption peak
higher ν_0(shorter λ_0)→larger Abbe number
(smaller dispersion)

Pb^{2+}, Ti^{4+}, Nb^{5-}, Ba^{2+}, La^{3+}, Y^{3+}, Th^{4+}, Ta^{5+} ions provide large refractive index.

$Pb2^{+}$, Ti^{4+}, Nb^{5+} : Large dispersion
Absorption peak→longer wavelength
Ba^{2+}, La^{3+}, Y^{3-}, Th^{4+}, Ta^{5+} : Small dispersion
Absorption peak→shorter wavelength

表 2.3　光学ガラスの物理化学的特性

	n_d	ν_d	熱的性質		化学耐久性*	
			Sp	$\alpha\times10^7$	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	451	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	91	1	2
K 8	1.51276	59.8	512	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	2
SK 1	1.61025	56.5	680	76	4	2
SK 3	1.60881	58.9	689	76	5a	2
SK 5	1.58913	61.2	680	72	4	2
SK 16	1.62041	60.3	672	75	5b	3
PK 1						
BK 1	1.51009	63.4	610	92	1	2
BK 7	1.51680	64.2	612	88	1	1
PKS 1	1.51728	69.6	515	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	581	77	5a	2
LaF 3	1.71700	47.9	668	93	5a	1
LaK 10	1.72000	50.3	650	74	5a	2

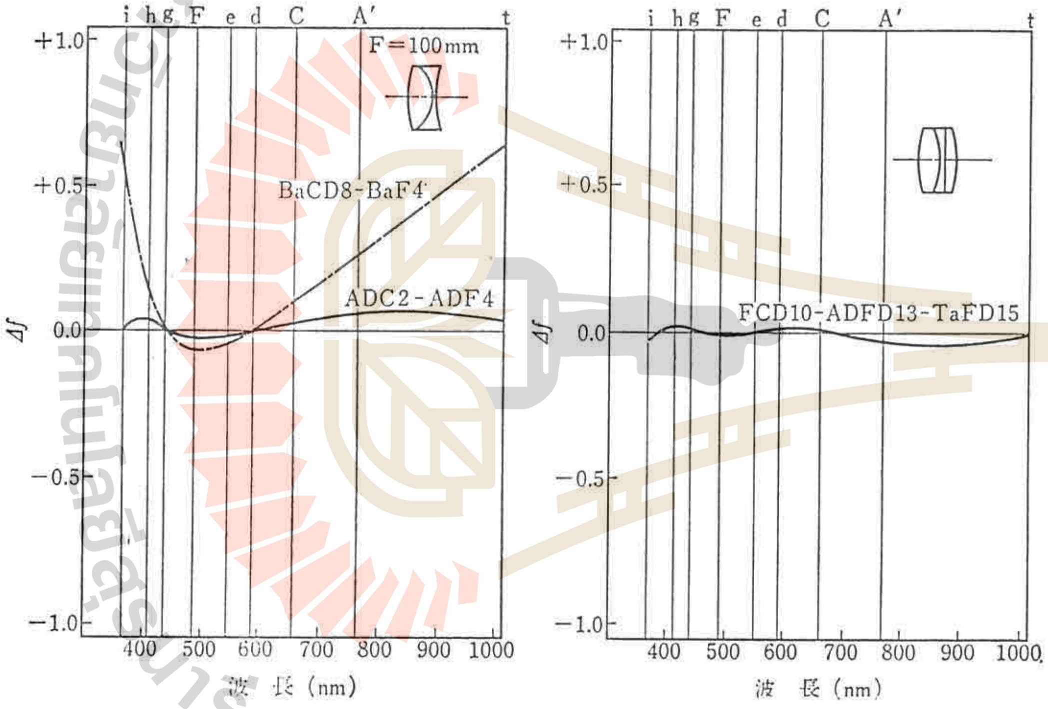
注（1）　耐酸性については 1/100 *N*　HNO_3 150 *ml* 中に 50 C で1時間浸漬し，その重量減パーセントによって分類

級	Da 1	Da 2	Da 3	Da 4	Da 5
重量減%	<0.03	0.03～0.10	0.10～0.30	0.30～1.00	1.00<

注（2）　耐水性は粗砕ガラスを一定量の蒸留水中に一定時間煮沸して，重量減%を測定

級	Dw 1	Dw 2	Dw 3	Dw 4
重量減%	<0.05	0.05～0.20	0.20～0.50	0.50～1.00

＊　新しい測定法とデータは §2.2.C および表2.10に記載



(a)

(b)

図 5.4 超色消しレンズの収差特性の 例 （a）ADC2-ADF4 （b）FCD10-ADF8-TaFD15

As a result, Ti^{4+} and Pb^{2+} provide high refractive index and high dispersion, La^{3+}, Gd^{3+}, Y^{3+}, Zr^{4+} and Ta^{5+} give high refractive index and low dispersion, and P_2O_5 and F^- provide low refractive index and low dispersion.

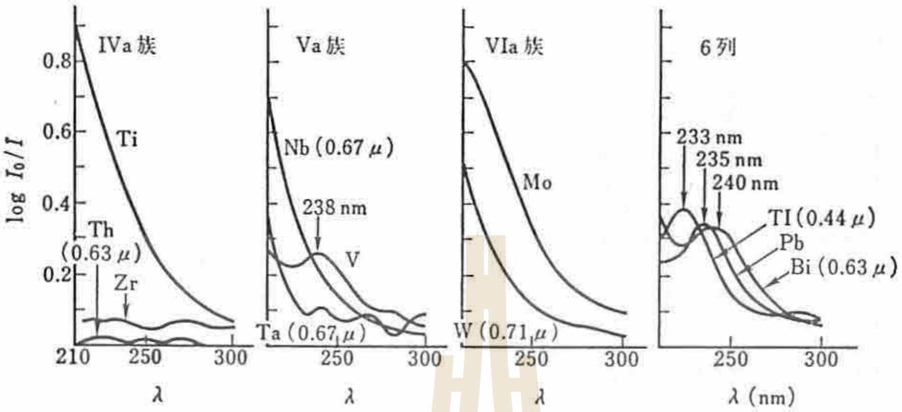


図 2.5 紫外光域における $BO_{1.5}$ 80, BaO18, MOn2 ガラスの吸収

Next step is of the making decision of glass forming region. Usually the glass forming region can be determined by using three component triangle: i.e. glassformer-specified oxides(above component)-alkali/alkaline earth oxide. In these glass-forming region the most stable and specified optical constant of glasses should be selected.

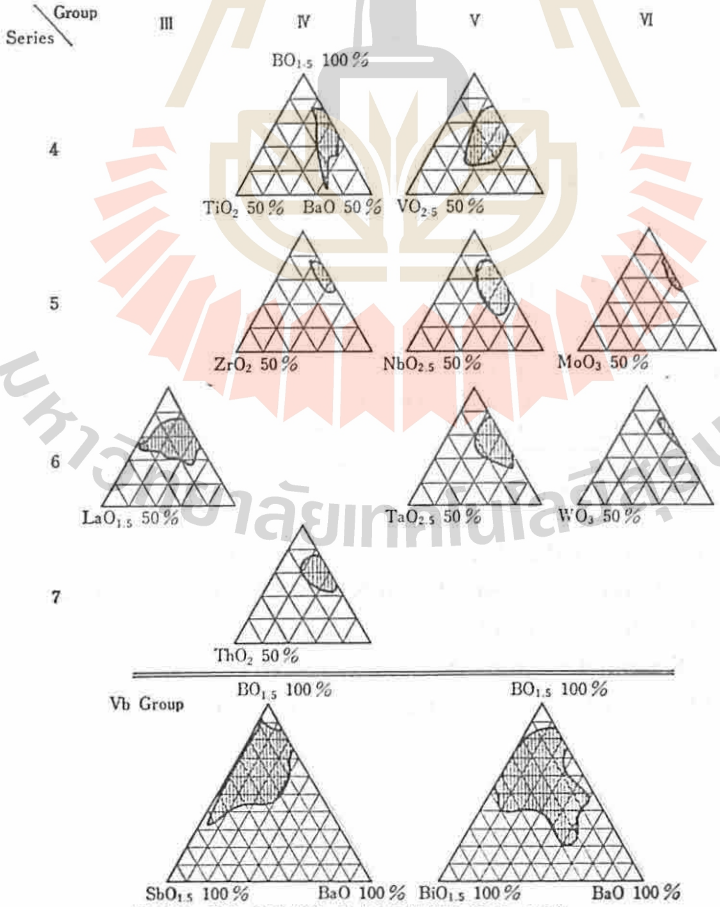


図 2.31 B_2O_3-BaO-MOn 系ガラス化領域 (Cationic%)

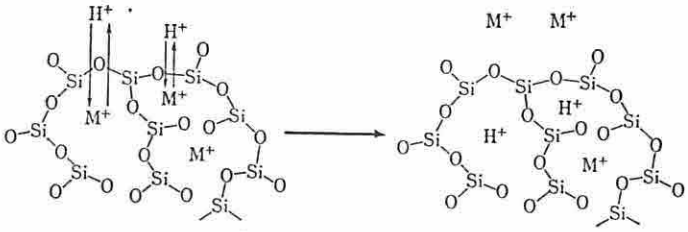


図 2.34　ガラスと水の反応

表 2.13　光学ガラスの化学耐久性

	D_0	T_{Blue}	D_w	D_{NaOH}	D_{STPP}		D_0	T_{Blue}	D_w	D_{NaOH}	D_{STPP}
FC 5	7.5	5.0	0.54	0.15	0.02	BaF 3	<0.3	>70	0.02	0.05	<0.01
BSC 7	<0.3	>70	0.21	0.06	<0.01	BaF 10 N	<0.3	>70	0.02	0.03	<0.01
C 3	<0.3	>70	0.15	0.04	<0.01	BaF 11 N	<0.3	>70	0.02	0.02	<0.01
CF 6 N	<0.3	>70	0.06	0.02	<0.01	BaF 13	5.0	—	0.08	0.22	0.05
FEL 2	<0.3	>70	0.09	0.04	<0.01	BaF 22 N	0.4	†	0.02	0.02	<0.01
FEL 6	<0.3	>70	0.05	0.03	<0.01	BaFD 2	1.6	†	0.03	0.07	0.04
FL 5	<0.3	>70	0.04	0.05	<0.01	BaFD 7 A	<0.3	>70	0.02	<0.01	<0.01
FL 7	<0.3	>70	0.04	0.05	<0.01	BaFD 8 N	<0.3	>70	0.02	<0.01	<0.01
F 1	0.4	>70	0.03	0.08	<0.01	BaFD 15	<0.3	>70	0.03	<0.01	<0.01
F 2	0.6	70	0.03	0.06	<0.01	LaCL 2	45.0	2.0	0.80	0.94	0.85
F 4	<0.3	>70	0.04	0.05	<0.01	LaCL 5	40.0	3.5	0.11	0.06	0.29
F 5	<0.3	>70	0.04	0.05	<0.01	LaCL 6	50.5	†	0.44	0.49	0.93
FDS 3	5.0	†	0.05	0.12	0.07	LaCL 7	27.0	3.5	0.56	0.12	0.69
FD 1	2.6	†	0.03	0.11	0.04	LaC 8	5.3	†	0.02	<0.01	0.27
FD 2	1.1	70	0.01	0.07	0.02	LaC 9 N	11.0	†	0.02	0.03	0.65
FD 4	4.5	†	0.03	0.11	0.12	LaC 10	4.5	10	0.03	<0.01	0.42
FD 5	1.0	70	0.04	0.09	0.02	LaC 11	42.5	2.0	0.02	0.17	0.19
FD 6	11.2		0.02	0.16	0.26	LaC 12	47.8	1.0	0.14	0.15	0.79
FD 3	1.3	70	0.04	0.08	0.04	LaC13N	5.4	10	0.04	0.01	0.22
FD 10	0.3	>70	0.03	0.08	<0.01	LaC14A	5.1	†	0.01	0.01	0.15
FD 11 N	1.3	†	0.01	0.14	0.03	TaC 6	3.3	70	0.01	<0.01	0.03
FD 13	1.0	†	0.03	0.08	0.02	LaFL 2	116.0	0.8	0.25	0.31	0.38
FD 14	0.5	†	0.01	0.10	<0.01	LaFL 3N	4.6	45	0.03	0.02	0.01
FD 15 N	0.5	†	0.04	0.08	<0.01	LaFL 5 N	2.0	45	0.01	<0.01	0.01
BaCl	2.2	10	0.06	0.08	<0.01	LaFL 6 N	0.9	72	0.01	<0.01	<0.01
BaC 4 N	0.3	>70	0.02	0.03	<0.01	LaF 2	2.5	25	0.03	<0.01	0.02
BaCD 2	1.5	25	0.09	0.09	0.02	LaF 3 N	5.7	45	0.04	<0.01	0.04
BaCD 4	4.7	6.0	0.06	0.21	0.01	NbF 1	5.0	10	0.01	<0.01	0.33
BaCD 5	2.0	10	0.12	0.15	<0.01	NbFD 3	1.9	25	0.06	<0.01	0.14
BaCD 7	4.7	5.0	0.12	0.24	<0.01	NbFD 10	1.6	25	0.02	<0.01	0.03
BaCD 10	7.8	5.0	0.03	0.33	0.04	NbFD 11	2.7	25	0.02	<0.01	0.12
BaCD 14	17.0	2.0	0.13	0.34	0.04	NbFD 12	1.9	25	0.01	<0.01	0.07
BaCD 15 N	11.0	10	0.09	0.07	0.05	NbFD 13N	1.4	45	0.02	<0.01	0.02
BaCD 16 N	23.4	†	0.07	0.71	0.89	TaF 1 A	2.4	70	0.01	<0.01	0.02
BaCD 18N	9.9	10	0.03	0.08	0.05	TaF 3 A	1.2	70	0.01	<0.01	0.02
BaCED 4	3.8	10	0.07	0.16	0.02	TaFD 1N	2.5	70	0.01	<0.01	<0.01
BaCED 5N	1.0	25	0.02	0.03	<0.01	TaFD 5	0.4	70	0.01	<0.01	0.02

（注）†…ガラス表面全体が溶解するために青色の青ヤケ層が観察されない硝種，または青色の干渉色の変化が不規則な硝種

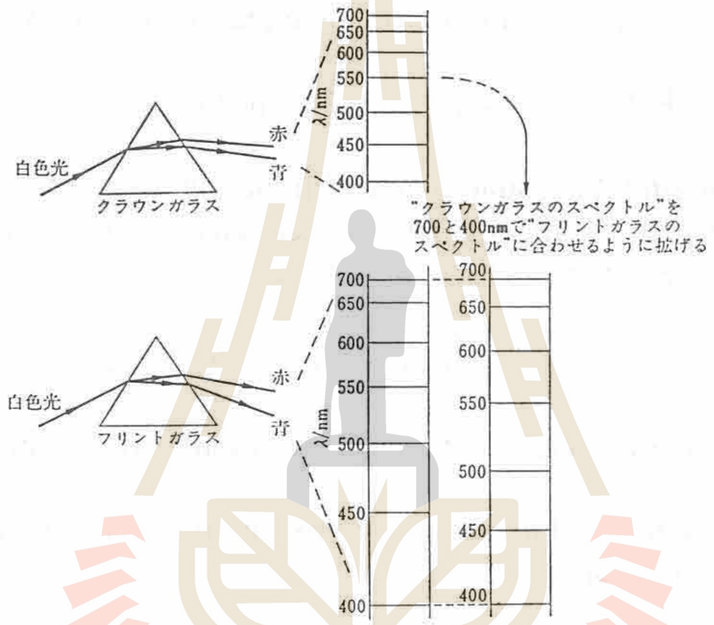
Do : True water durability(mg/cm^2·Hr), 50°C
T_{Blue} : Time required blue interference color formation(Hr)
D_W : Weathering durability(mg/cm^2·Hr)
D_{NaOH}: Alkaline durability(mg/cm^2·Hr), M/100-NaOH, 50°C
D_{STPP} : Detergent durability(mg/cm^2·Hr), M/100-$Na_5P_3O_{10}$, 50°C

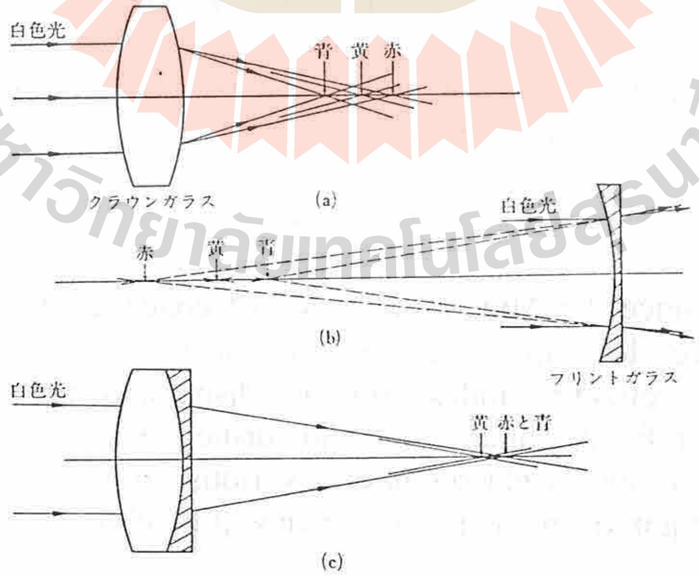
(3). Chemical Durability of Optical Glasses

The chemical durability of optical glasses is a very important property. In particular the optical glasses have special compositions compared to other glass products. Optical glasses must be fabricated to lenses and prisms subsequently. In fabrication processes, glasses contact with water, sometimes with alkaline solution, and frequently are attacked by these solutions.

3. Lens Design

A number of formula derived from the simple thin lens formula are used to show how lens design has been affected by the availability of a wide range of optical glasses. “Real life” lens design is a complicated





business and nowadays makes considerable use of digital computers.

The thin formula giving the focal length in terms of the refractive index of the glass and the radii of curvature of the lens surface is

$$1/f = (n-1)\cdot(1/R_1 - 1/R_2) = K(n-1)$$

The focal length of f_T of a doublet, i.e. two simple lenses mounted together is given by

$$1/f_T = 1/f_1 + 1/f_2 = K_1(n-1) + K_2(n_2-1)$$

where f_1 and f_2 are the focal length of the constituent lenses.

If the doublet is to have the same focal length for the C and F wavelength, i.e. $f_{TC} = f_{TF}$, the following equation must be satisfied

$$K_1(n_{1C}-1) + K_2(n_2-1) = K_1(n_{1F}-1) + K_2(n_{2F}-1)$$

By rearranging this equation and eliminating K_1 and K_2 by making use of the formula for the focal length of each lens for the He-d line, it is easy to show that the condition for achromatism is

$$\nu_1 f_{1d} - \nu_2 f_{2d} = 0 \ [\text{ or } \Sigma(1/\nu_i f_i) = 0,\ \nu_1/\nu_2 = f_2/f_1]$$

From this equations one begins to appreciate the significance of the Abbe number.

For a lens to produce a flat stigmatic image the so-called Petzval condition must be satisfied

$$n_{1d}\cdot f_{1d} - n_{2d}\cdot f_{2d} = 0 \ [\text{or } \Sigma(1/n_k\cdot f_k)=0,\ n_1/n_2 = f_2/f_1]$$

Therefore the following condition must be satisfied to eliminate both achromatic and stigmatic aberration.

$$n_1/n_2 = \nu_1/\nu_2$$

In general, since the Abbe number, ν_1, of concave lens is smaller than that of convex lens, $n_1 > n_2$, i.e. both n_1 and ν_1 are large, a convex lens having high refractive index and low dispersion and a concave lens having low refractive index and high dispersion, should be combined. Therefore, the optical glasses having various refractive index and Abbe number is required, and there are so many kind of optical glasses.

4. Filters

The filters which absorbs specified wavelength of light can be used for optical systems. There are many kind of filters:

①. UV transmission filter
②. Sharp-cut filter
  Colorless, Yellow, Orange, Red
③. IR transmission filter
④. Blue filter
⑤. Green filter
⑥. Chromatic temperature conversion, chromatic compensate filter
⑦. Neutral density filter
⑧. IR absorbing filter
⑨. UV transmission and visible absorbing filter
⑩. Others

(1). Filters Absorbing Shorter Wavelength than Specified Wavelength

These filters include (1) to (3) of above category and absorb the light below specified wavelength. The band-gap of silica glass is about 10eV, hence the silica glass has a sharp absorption peaks around 107 and 120nm. The addition of alkali oxide into silica glass shifts this absorption peak toward longer wavelength. As Ti, Nb and Ta are added into silica glass, the peak around 5ev appears, as a result, the light of wavelength shorter than 300nm can be absorbed. These glasses can be used for UV absorbing filter.

Further longer wavelength absorbing filter is realized by using a semiconductor which has small band gap. CdS-CdSe solid solution can be applied for this purpose. As shown before, as increase in the amount of CdSe(Se) increases the wavelength of absorption.

(2). Filters Absorbing Specified Wavelength

The transition metal ions can be introduced into the glass for absorption. The UV transmission filter is made by the adding these transition metal ions.

Neutral density filter absorbs whole visible light.

5. Optical Glass-Production

The process of optical glass production consists mainly of (1)Melting, (2) Forming and (3)Annealing process. The optical glass differs markedly from other glass products in the point of homogeneity, i.e. no distortions, free of bubbles, no stresses. The technical efforts have been concentrated only on the homogenization in the melting process to eliminate distortions(striae) and bubbles.

The pressing process follows by melting. Recently, the direct pressing method can be applied. The lens blanks is fine-annealed to compensate the refractive index with specified value.

The manufacturing process of optical glass has changed markedly in 1965 from conventional batch process to modern continuous process. The process of binocular prisms production has been established and it can be produced by continuous process. And the photographic lenses can also be produced after 1971 by 3D method(Direct melting, Direct pressing, Direct annealing).

(1). Raw Materials, Melting, Stirring

High quality(high purity) raw materials should be used for optical glass production. For example, the iron content of sand is limited below 0.005 %. Usually, a high quality chemicals are applied.

In conventional process, the fire clay crucible has been used for melting. There were many problems resulting from the crucible:

①. Corrosion of crucible by molten glass(leak of glass)
②. Generation of bubbles(pores of crucible)
③. Generation of striae(corrosion of crucible)
④. Spoling(cooling of crucible out side the furnace)
⑤. Coloring(impurities of crucible, corrosion of crucible)

The "stirring" is the characteristic and special technology used for only optical glass production. Many researches have been done on the stirring of optical glass. Since the fire-clay crucible has been used for the melting of optical glasses up to 1945, the corrosion of crucible was unavoidable. Therefore, the purpose of stirring was the collecting of the striae to the center or the wall portion of the crucible, not to be distributed the striae. And only the portion of glass between these should be taken out as a homogeneous glass. As a results, the yielding of melting only less as 40%.

However, after 1945, only the striae resulting from the volatilization of some components must be considered, the selection of various shapes of stirrers can be allowed to consider by using Platinum crucible.

After the World War II, the new glass system of La-containing has been developed. Since the fire-clay crucible could not be used for the melting of this glass because of the marked corrosion of crucible, the platinum crucible must be used for this purpose.

The next table shows the comparison of the manufacturing process of optical glass.

Here we can compare the each melting method.

①. Fire Clay Crucible

Fire clay crucible has been used for optical melting for a long time (17th century to middle of 20th century). In this method, the fire clay crucible was taken out from the furnace after melting of glass and was cooled down by water. Therefore, the most important factor in this method is how to make the anti-corrosion and anti-spoling crucible. Fire clay crucible includes many pores, which becomes the generation of bubbles, and provides the coloration by iron impurity. As a result, it is difficult to obtain the yield of melting over 40 %.

Clay Crucible →	Pt. Crucible →	Platinum Tank	
Batch	Batch	Continuous	
Block	**Casting**	**Strip**	**Direct Press**
Crucible Making (120 days)	Pt. Crucible	Platinum Tank	Platinum Tank
propane gas	Gas,Electric(SiC)	Electric(direct)	Electric(direct)
Pre-firing 5days			
Firing 1	Melting	Melting	Melting
Melting 1	Casting 1/2days	Forming	
Cooling 7	Cooling 5	(Strip) 1day	
Crushing 1	Cutting 1/2	Cooling	
Checking 3	Polishing 3		
Forming 5			2days
Polishing 3			
	Check 1		
	Cutting 1		
	Press		Press
Products	Anneal 21		Anneal
	Inspection 1		Inspection 1day
	Products		Products
Total 170days	34days	25days	3days
Yield 40 %	70 %	90 %	90 %
(Melting)			(Products) Max.

②. Pt or Pt-alloy Crucible

Lanthanum-borate glass has a extremely low viscosity of few to few tenth poise, it behaves as water. Therefore, the Pt or Pt-alloy crucible must be used for melting of this glass. The wettability between glass and the surface of crucible is well, and free of pores. The corrosion of crucible by molten glass is negligible. By these advantage of this crucible, the rotation(rpm) of stirring increases as possible, the striae free glass can be obtained compared with fire clay crucible. However, since this method is batch system, it is not suitable for mass production.

③. Continuous Melting(Pt or Pt-alloy Tank)

The continuous melting has been tried in Baush & Lomb or Corning around 1960. In 1964 Hoya glass Co. succeeded in continuous melting of optical glass, BK7.

The following table shows the differences of refractive index between homogeneous part and striae part.

表 3.1　種々のガラスの脈理の屈折率差　　　a：脈理の厚さ

		A	B	C	D
BK 7	a Δn	2.12mm -5.2×10^{-5}	3.86 -7.1×10^{-5}		1.66 -1.6×10^{-4}
F 2	a Δn	1.64mm -1.0×10^{-4}	2.50 -1.1×10^{-4}	2.44 -4.5×10^{-5}	4.59 -3.0×10^{-5}
F 16	a Δn	2.26mm $+3.6\times10^{-5}$	3.33 $+4.9\times10^{-5}$	2.44 $+3.4\times10^{-5}$	3.97 $+2.8\times10^{-5}$
LaK 12	a Δn	0.64mm $+1.7\times10^{-4}$	1.66 $+5.8\times10^{-5}$		

There are many types of stirrers:

- (1). Rod type
- (2). Crank type
- (3). Propeller type
- (4). Vertical propeller type
- (5). Spiral type

Many researches have been done on the efficiency of the shape of stirrers, it was found that the crank type was available for low viscosity glasses, and the spiral type was effective for higher viscosity of glasses.

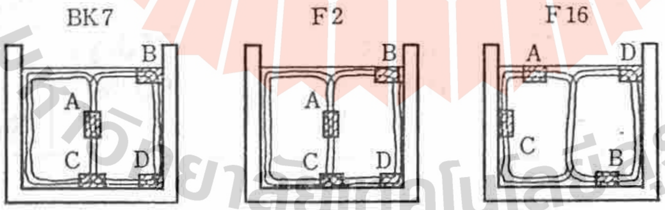


図 3.5　粘土るつぼ中の脈理分布例

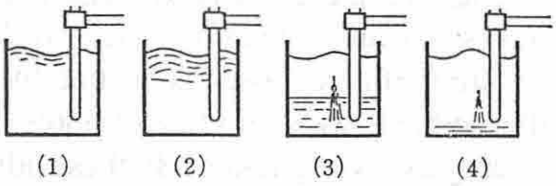


図 3.6　従来のロッド型攪拌棒による液の流れ (60 r.p.m)

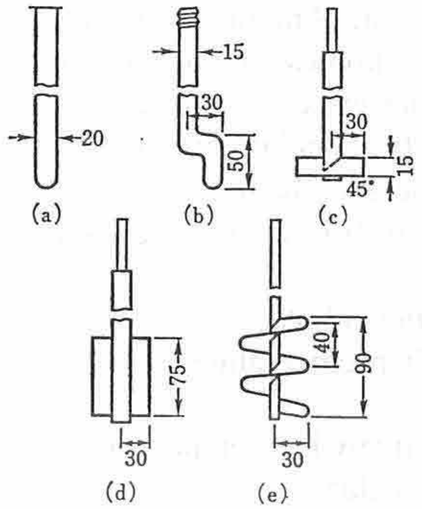


図 3.7 攪拌棒の形状と寸法 (mm)

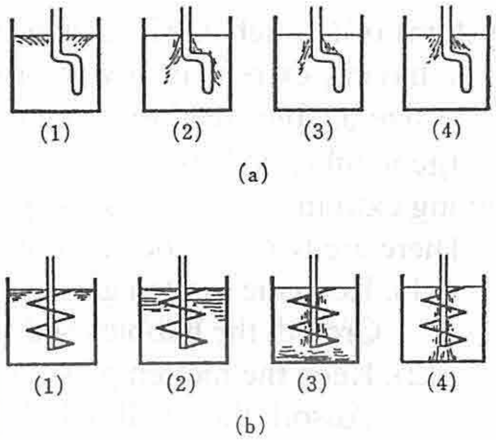
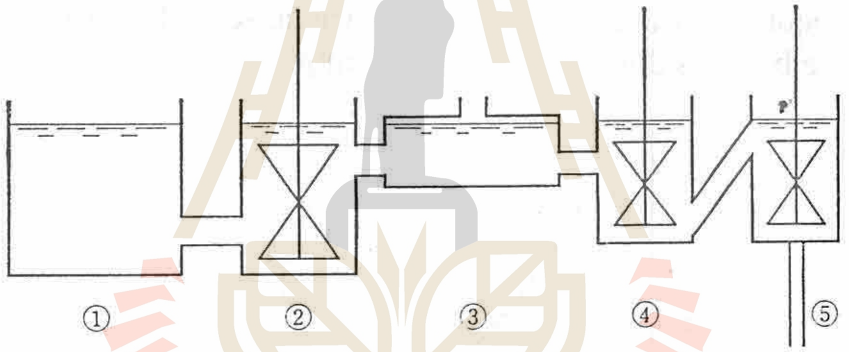


図 3.8 クランク型，螺旋型攪拌棒による液の流れ (60 r. p. m)

Next figure shows the schematic representation of continuous tank melting process for optical glass. This consists of many chambers, such as melting, refining, stirring, working chambers, etc., and are combined with a unit operations of each processes.



Although the propane gas has been used for melting of optical glass for a long time, the glasses can be melted by direct electrical boosting from around 1975. Especially, this technology has a high efficiency of heat and to avoid pollution in small tank furnace. The melting ability of this method is 0.4~0.55m^2/ton/day, and the efficiency of heat is as high as about 20 % (gas firing:3~4 %). The electrode widely used is SnO_2.

(2). Refining

One of the important factor determining the yield of optical glass manufacture is the bubbles. The reduction of bubbles of glass articles might be the technical subject in all glass melting. In particular, the bubbles of over 50 μm is not permissible for optical glasses. For example, the number of bubbles of 30μm presented in BK7 glass is only less than 0.3/1Kg of glass.

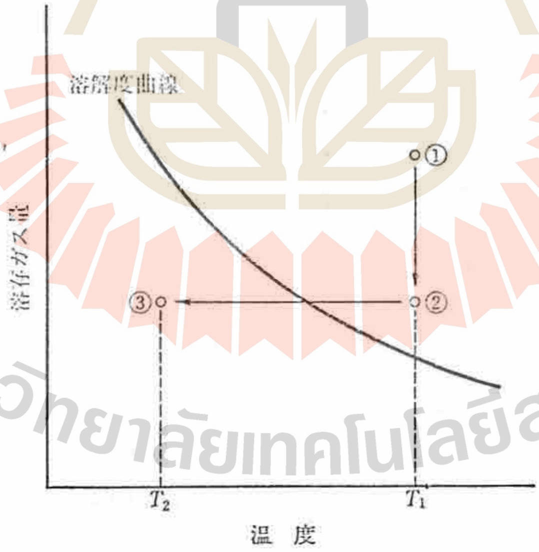
It was surprised that the components of bubbles consist of gases from the raw materials decomposed, not air. Among over 200 of optical glasses, the relatively large number of bubbles tend to remain in the glass systems of (1)such as KF having higher viscosity and (2)such as La- and SSK having extremely lower viscosity. A relatively small number and large size bubbles tend to remain in the glass having higher viscosity, and a large number and small bubbles below 10µm tend to remain in the glass having extremely lower viscosity.

There are two methods to remove the bubbles.

(1). Keep the molten glass at higher temperature
Growth the bubbles and rise up
(2). Keep the molten glass at relatively low temperature
Absorb the small bubbles into glass

These methods are based on the diffusion rate and solubility curve of gases dissolved in glass.

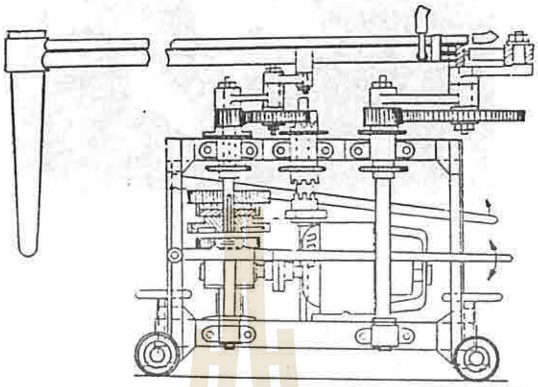
The refining of optical glasses would proceed as follows: supersaturation of gas is now maintain at T_1 after melting of glass. At ① the gases form and grow and these gases can be removed from molten glass and transits to the state ②. Then the glass was cooled to T_2, the gases becomes to unsaturated ③ and was absorbed into glasses. At this point, the bubbles does not form by stirring.



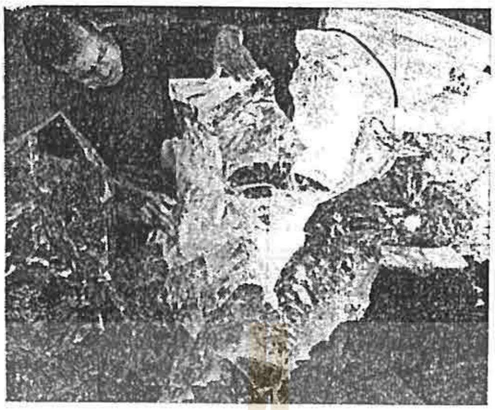
The removing of bubbles of over 200 of optical glasses is not simple, but it depends on the occasion.

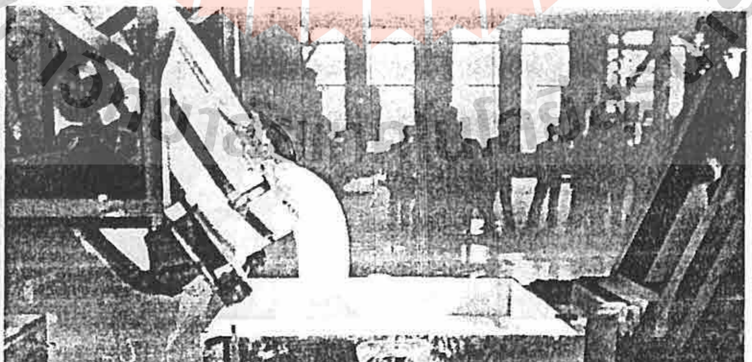
(3). Shaping and Forming

The mold in pressing process usually is made by cast iron, steel and Cr-steel, etc. Because of low thermal conduction of glass, there are many problem, share-mark etc. The pressed lens blanks requires the subsequent process, annealing, lapping and polishing.

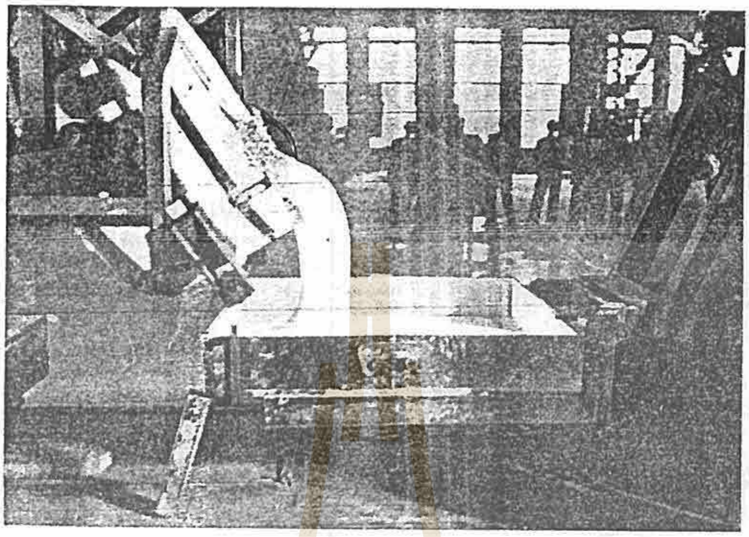


(Eckert)

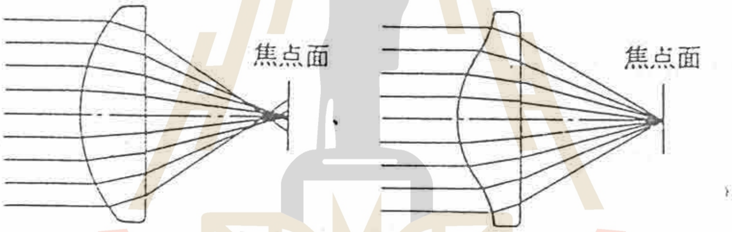




A large telescope lenses, telescope mirror blanks and filters can not be produced by these small glass blocks. The casting has been applied for this purpose. The homogeneous molten glass is poured in the mold, and then was cooled carefully with mold.



2．光学ガラスの鋳込みの実況
（日本光学工業ＫＫ提供）



(a) 球面レンズ　(b) 非球面レンズ

(4). Direct Molding Technology

In 1982, Eastman-Kodak has developed an epoch-making technology. This was the mass-production of aspherical glass lens by direct molding technology. In those days, though the spherical lenses was capable to be produced by conventional lapping and polishing, the fabrication of aspherical lens was seemed to be quite difficult. Aspherical lens provides to eliminate spherical aberration.

The direct mold technology has many advantages:

①. No grinding, lapping, polishing
②. Possible to produce aspherical lens
③. Both concave and convex lens
④. Capable of small lenses

These glass mold lenses can be used in many field: video camera, CD (automobile), laser-beam printer, compact camera, optical disk, bar-code reader, reflex camera, optical-communication, CCTV, etc. The manufacturing process of direct mold lens is as follows:

Re-Heat Press Process	**Direct Press Process**
Preparation of Batch ↓ Melting Cast ↓ Annealing ↓ Inspection and Selection of Blocks ↓ Cutting ↓ Weight compensation ↓ Re-heat ↓ Pressing and shaping($\eta=10^4$Pa·s) ($1\sim20$Kg/cm^2) ↓ Fine annealing ↓ Final inspection ↓ Products	Preparation of Batch ↓ Melting ↓ Flow compensation ↓ Cutting ↓ Direct pressing($\eta=10^2$ Pa·s) ($1\sim20$Kg/cm^2) ↓ Fine annealing ↓ Inspection ↓ Products

Direct Molding Process
Preparation of glass pre-form ↓ Direct molding($\eta=10^7\sim10^{11}$Pa·s) ↓ Holding for enough time ↓ Removal of lenses($\eta=10^{10}\sim10^{11}$Pa·s) ↓ Fine annealing ↓ Products

The direct molding technology can be established by many advanced technology:

①. Development of new mold materials
②. Ultra fine fabrication technology of mold

③. Development of glasses or pre-form capable of molding
④. Ultra fine fabrication technology
⑤. Measurement and testing technology of aspherical lens
⑥. Optical system design including aspherical lens

The following materials are used as mold:

1. Glassy carbon(C)
2. Silicon carbide(SiC)
3. Silicon nitride($S1_3N_4$)
4. Tungsten carbide(WC)
5. Various kind of cermet
6. Thin film coating of noble metal alloy(Pt-alloy)
7. Diamond and diamond thin film coating
8. Various carbide, nitride and botide
9. Cr_2O_3 ceramics(Cr_2O_3:86, ZrO_2:10,TiO_2:4 wt%)

At least almost of all optical glasses are capable of direct molding in a laboratory scale. However, the appropriate glasses capable of direct molding at relatively low temperature can be selected in a mass production.

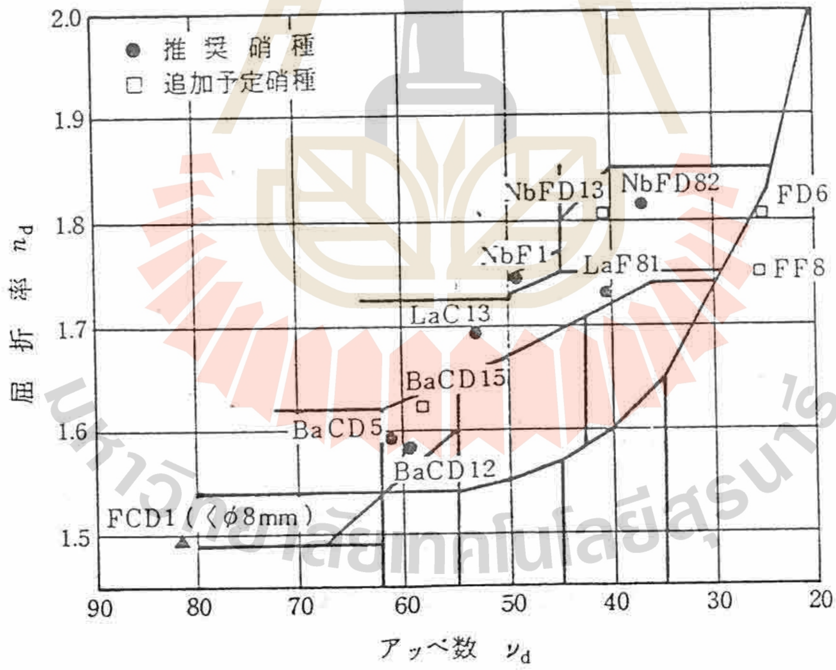
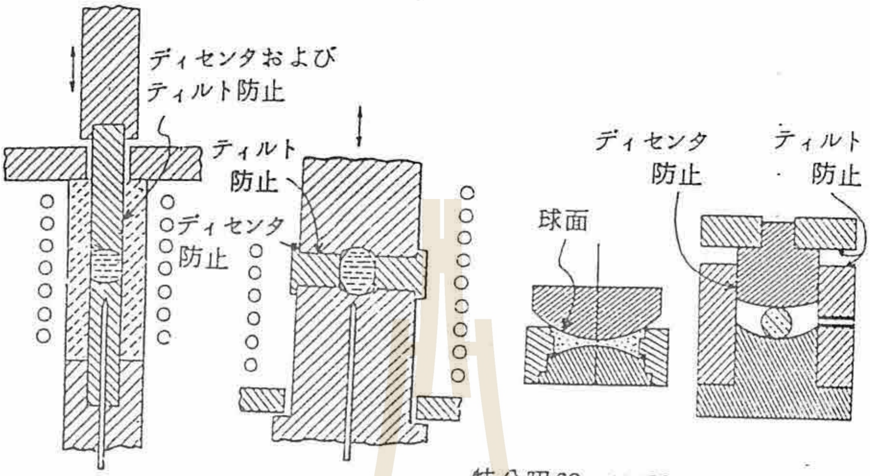


図3　HOYAのガラスモールド用光学ガラス
（FCD 1 以外は頭文字として"M-"が付加される）

The sufficient accuracy of shape and size of direct molding lenses are satisfied.



USP　4481023
（コーニング）

特公昭62－41180
（キヤノン）

USP　4836840
（HOYA）

図8　型構造の例

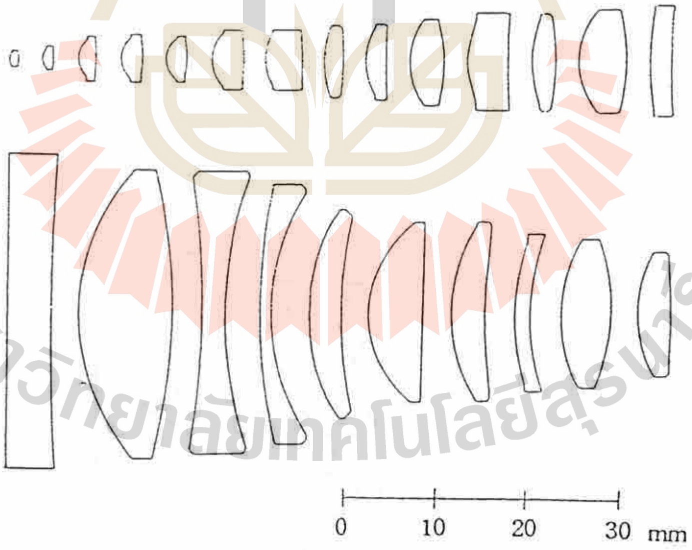


図7　HOYAで生産された種々のレンズ

(5). Annealing

The annealing of optical glass is a significant process, and it acts four important roles:

①. Remove the residual stress
②. Provide the refractive index in whole glass products (homogeneous refractive index)
③. Elimination of scatter of refractive index among the glass
④. Provide the refractive index to specified value

There are two method of annealing for optical glass: (1)constant rate cooling method, (2)constant temperature keeping method.

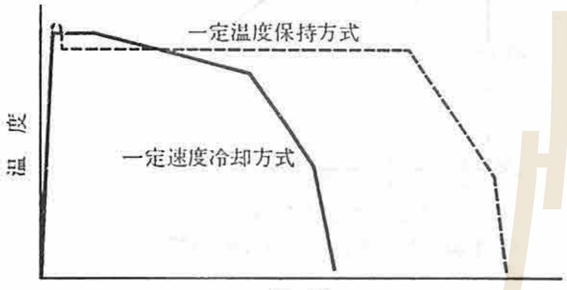


図 3.24 徐冷方式

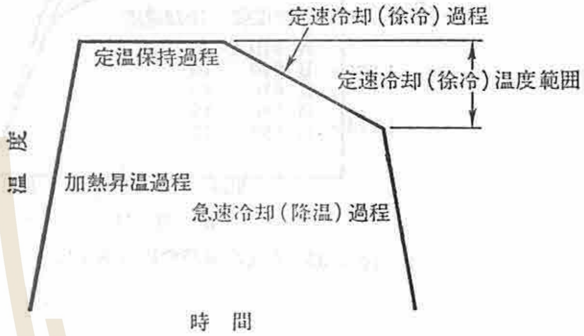


図 3.25 徐冷スケジュールの各過程

In former method, the glass was held at relatively high temperature(e.g. Tg) and was cooled at constant rate. In this process glass would have a specified configurational structure which provides a constant refractive index. In the latter method, the glass was held for a long time at constant temperature, and was cooled gradually to avoid thermal stress. Recently, the former method is widely used to obtain a good homogeneity and to save the processing time. The annealing schedule consists of heating, soaking, slow cooling and rapid cooling steps. Among these steps the soaking process and constant rate cooling process are the most important.

The change in refractive index by heat treatment has been discussed in some detail previously.

(6). Grinding, Lapping, Polishing

In conventional lens manufacturing process, following three processes have been required.

①. Diamond Grinding

In a diamond grinding process, the glass removal mechanism are

Diamond Grinding(Curve generator, roughly shaping)
↓
Lapping(Smoothing the surface, SiC abrasive powder)
↓
Polishing(Optical surface, Pitch and CeO_2 powder)

表 3.9　LF 6, BCL-8 の特性値

	軟化点（$10^{7.6}$ポアズ）	屈伏点（10^{10}ポアズ）	転移点（$10^{13.5}$ポアズ）	歪点（$10^{14.5}$ポアズ）
BCL-8	668 ℃	610 ℃	578 ℃	566 ℃
LF 6	630 ℃	479 ℃	420 ℃	390 ℃

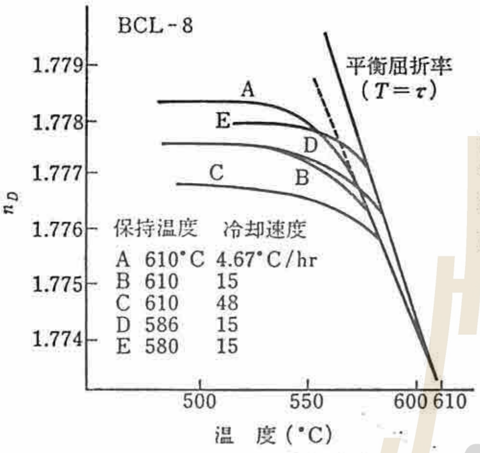


図 3.32　定速冷却時の屈折率変化

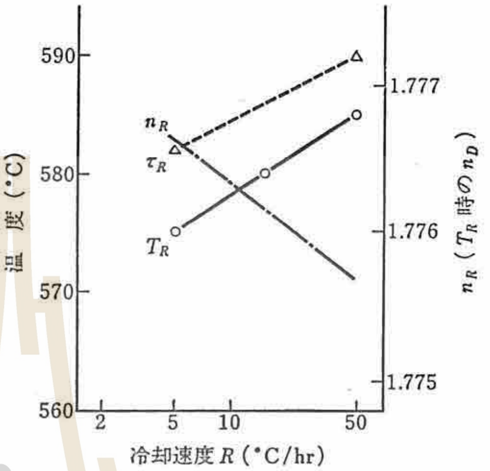


図 3.33　冷却速度と T_R, τ_R, n_R の関係(BCL8)

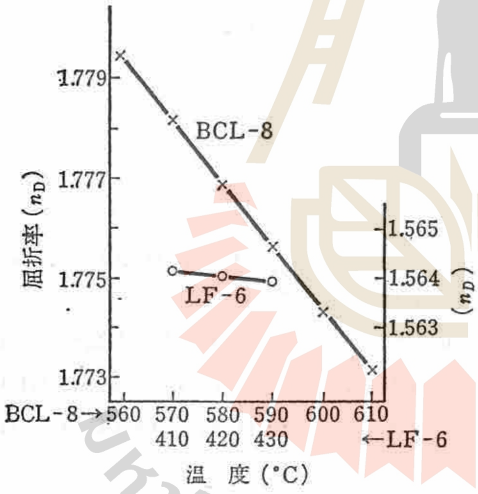


図 3.27　平衡屈折率と温度の関係

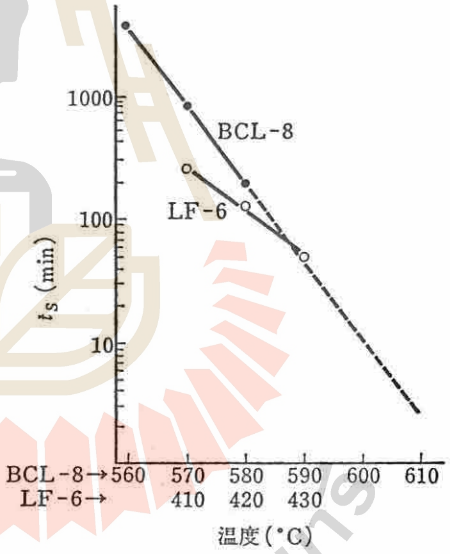


図 3.28　平衡到達時間と温度の関係

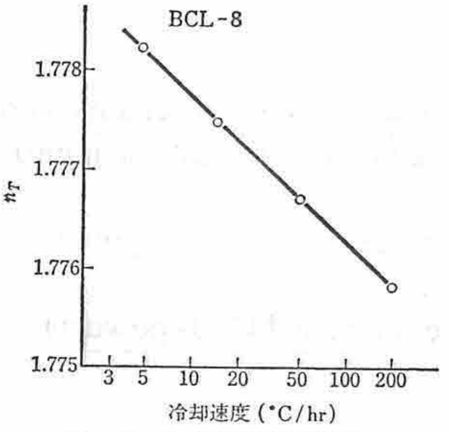


図 3.36　n_T と冷却速度の関係

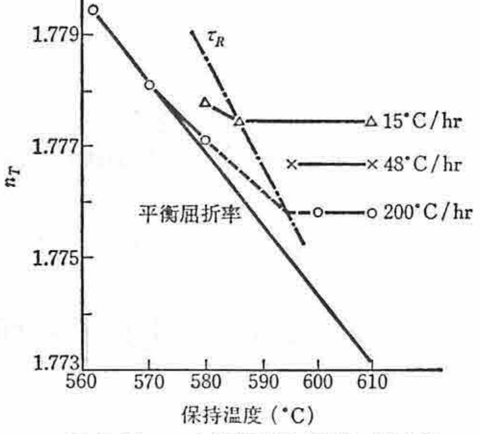


図 3.37　n_T と保持温度の関係（BCL8）

different depending upon the kind of glass. There are three types of glasses with different removal mechanism.

①. Glasses removed by fracturing: BK, SK, etc.
②. Glasses removed by scratching: TaSF
③. Glasses removed by both (1) and (2): SF etc.

The relationship between glass removal rate in diamond grinding and that in lapping with SiC abrasives is approximately linear. However, some glasses, SF glass for example, have low grinding rates in spite of high lapping rate. This is considered to be due to the fact that the glasses are removed by scratching in the grinding process, and by fracturing in the lapping process.

Glass removal rate during grinding decreases with the grinding duration. The change in glass removal rate is different for different glass types. This decrease in grinding rate is attributed not only to the wear of diamond grit but also to the absence or the decrease in dressing effect by glass fragment produced during the grinding process.

②. Lapping

The glass is lapped before polishing and the lapping hardness is a direct measure of its workability in the lapping process. However, the hardness of glass is usually expressed in terms of indentation hardness such as Vickers or Knoop hardness. What relationship are there between the lapping hardness and the indentation hardness? By what properties is the lapping hardness determined?

Indentation hardness of optical glass is an expression of micro-plasticity rather than and expression of densification. Lapping hardness is a measure of resistivity to fracture by lapping grains. Removing the effect of water, lapping hardness is dependent upon the indentation hardness and the intrinsic mechanical strength(or yield stress) of glass. There is an approximate but not strict, linear relationship between lapping hardness and Knoop hardness.

③. Polishing

The polisher

①. Must hold the polishing agents(CeO_2) in the interior.
②. Must have the function to transit the load pressure to the polishing grains
③. Must deform by itself or fit to the lapped glass surface geometrically

In order to satisfy conditions ① and ③, the polisher must be a viscous or an elastic material. In order to satisfy condition ②, it must have high rigidity. Therefore, the polisher is a visco-elastic or elastic material.

The elastic polisher(rubber) gives the ripple and the edge roll off. The visco-elastic polisher(pitch) gives the ripple free surface and lower creep compliance polisher(rosin) gives the edge roll off free surface. Polishing of a glass surface is brought about by the polishing grains in the polisher, cutting away the hydrated layer produced by the chemical reaction between the glass and the water.