

GLASSES FOR PHOTONICS

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1

Glass properties

Introduction

Glass can be made with excellent homogeneity in a variety of forms and sizes, from small fibers to meter-sized pieces. Furthermore, glass can be doped with rare earth ions and microcrystallites and a wide range of properties can be chosen to meet the needs of various applications. These advantages over crystalline materials are based on the unique structural and thermodynamic features of glass materials. Before discussing the special properties of glass, the fundamentals of glass materials are given in this chapter.

1.1 Features of glass as an industrial material

1.1.1 Structural features

1.1.1.1 Atomic arrangement

A glass is defined in ASTM [1] as ‘an inorganic product of fusion which has been cooled to a rigid condition without crystallization’. According to this definition, a glass is a noncrystalline material obtained by a melt-quenching process. Nowadays, noncrystalline materials that can not be distinguished from melt-quenched glasses of the same composition are obtainable by using various techniques such as chemical vapor deposition, sol-gel process, etc. Therefore, most glass scientists regard the term ‘glass’ as covering ‘all noncrystalline solids that show a glass transition’ regardless of their preparation method.

The words ‘noncrystalline solids’ and ‘glass transition’ suggest that a glass cannot be classified either in the category of crystalline materials such as quartz, sapphire, etc. or in the category of liquid. The atomic arrangement of a glass is different from those of crystalline materials and lacks long-range regularity, as schematically shown in Fig. 1.1 [2]. This is quite close to the

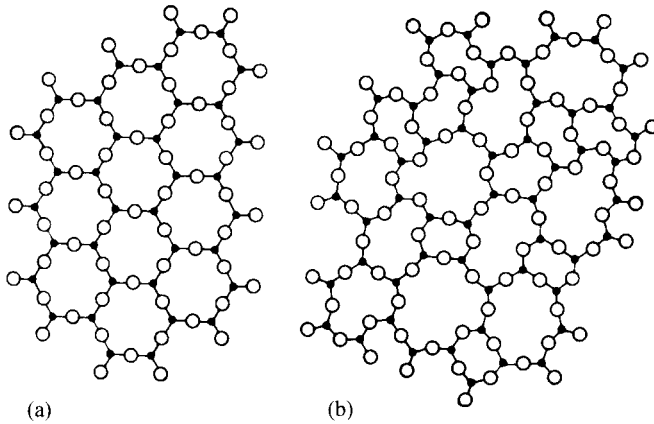


Fig. 1.1. Schematic two-dimensional illustration of the atomic arrangement in (a) crystal and (b) glass [2].

atomic arrangement in a liquid. There is neither crystal lattice nor lattice point in the glass structure and therefore, instead of diffraction peaks a halo is seen in the X-ray diffraction patterns of a glass.

Substances which can form noncrystalline solids with the atomic arrangement shown in Fig. 1.1(b) and at an appreciable size are found in oxide, halide, and chalcogenide systems. The three-dimensional random network of strong bonds is developed by the constituent called the ‘network former’. Some components called network modifiers can also participate in glass formation by acting to modify the glass properties. These components do not form networks but occupy thermodynamically stable sites as illustrated schematically in Fig. 1.2 or act as a replacement for a part of ‘network former’.

Glass formation is possible, in principle, for a system of any composition provided that it contains sufficient of the component called ‘network former’. Thus, a wide variety of multi-component glasses can be prepared to attain the desired properties by adjusting the chemical composition at a level below 1%. The lack of regularity of the atomic arrangement over a long range, i.e. the randomness of the structure, is essential to the understanding of the physical and chemical features relevant to those glasses which have the special properties that will be reviewed in this book.

The local environment of the modifying ions in Fig. 1.2 is different from site to site because of the lack in regularity of structure. Since an active ion doped in a glass occupies a similar position to the modifier ions, the absorption and emission spectra from the ion, if any, are broader than those from active ions

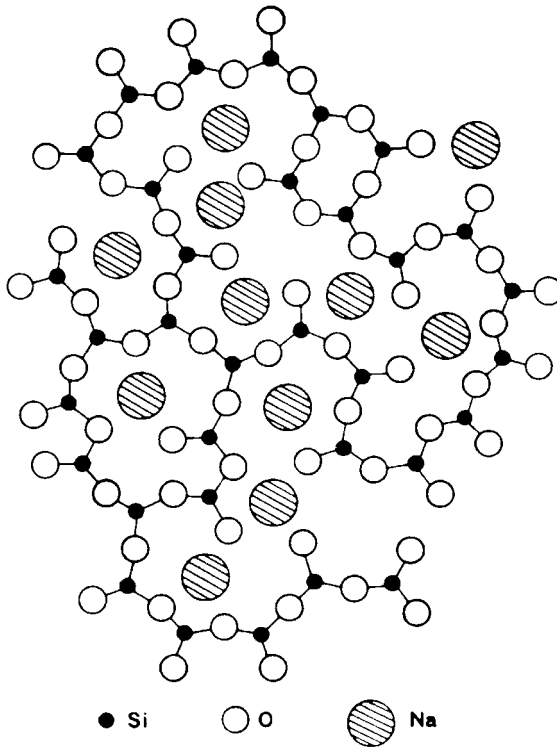


Fig. 1.2. Schematic two-dimensional illustration of the structure of a binary sodium silicate glass [3].

doped in a crystalline material as shown in Fig. 1.3 [4], a feature which is often advantageous in the preparation of a special glass.

The macroscopic properties of a glass such as optical transmission and absorption, refraction of light, thermal expansion, etc. are observed always equally in all directions, provided that the glass is free from stress and strain. That is, a glass is an isotropic material, whereas crystalline materials are generally anisotropic.

1.1.1.2 Chemical composition

Another important feature attributed to the uniqueness of the structure of glass is the flexibility of the chemical composition. Unlike crystalline materials, there is no requirement of stoichiometry among constituents provided that the electrical neutrality over the whole structure of a glass is maintained. Further-

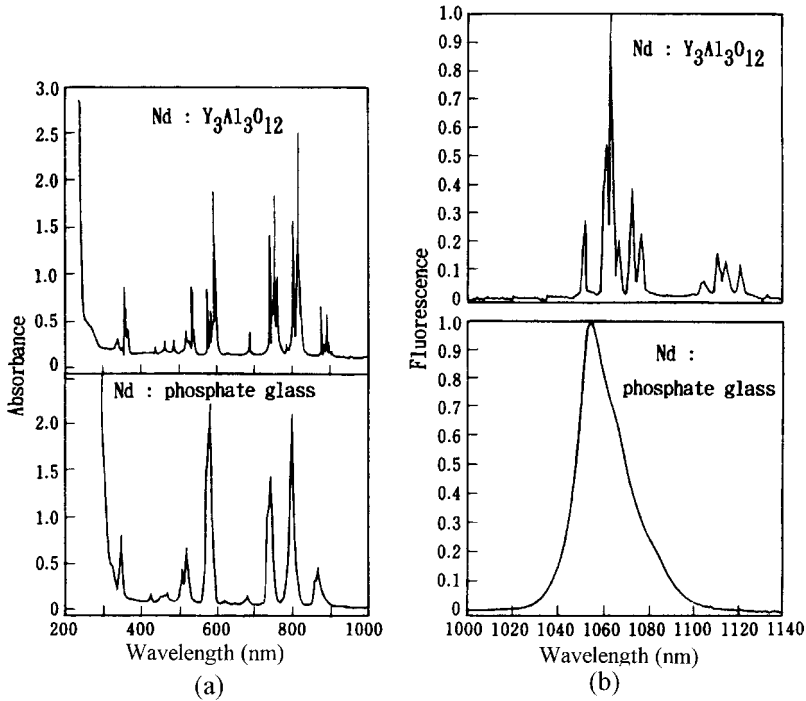


Fig. 1.3. Absorption and emission spectra of Nd ions in YAG crystal and phosphate glass. [Reprinted from M. J. Weber, *Handbook of the Physics and Chemistry of Rare Earth*, Vol. 4, ed. K. A. Gschneider, Jr. and L. Eyring (North-Holland Publishing Company, Amsterdam, 1979) p. 275.]

more, many properties of these multi-component glasses such as molar volume, thermal expansion coefficient, refractive index, etc. can be approximately described using the law of additivity of constituents [5]. These properties reflect the intrinsic nature of the respective constituents in proportion to their contents.

Property, P , of interest can be expressed approximately by Eq. (1.1) using the proportion of respective constituents, $f_1, f_2, f_3, \dots, f_i$, and factors representing their influence, $p_1, p_2, p_3, \dots, p_i$, as;

$$P = \sum p_i f_i = p_1 f_1 + p_2 f_2 + p_3 f_3 + \dots + p_i f_i. \quad (1.1)$$

As there is no requirement on the stoichiometric ratio among constituents it is easy to dope active elements such as rare-earth or transition metal elements, semiconductor components, etc. Thus we can obtain a glass which has the

unique properties inherent to the doped elements such as special color, emission of fluorescent light, high nonlinear susceptibility, etc.

The other feature that comes from the flexibility of glass composition is the ability to modify the properties of a glass through ion-exchange [6]. There are many stable sites for network modifier ions in a glass structure as shown in Fig. 1.2. For example, alkali ions that are easily thermally activated can move from one stable site to another within a glass. Such a movement of alkali ions within a glass structure enables us to replace alkali ions near the surface of a glass by other ions of the same valence, i.e. Na^+ by K^+ ; Na^+ by Ag^+ ; K^+ by Tl^+ , etc. This replacement of alkali ions in the original glass by other ions partially modifies the composition of the glass, and hence its properties. The technique, which will be described later in detail, is particularly important for the modification of optical and mechanical properties.

1.1.2 Thermodynamic features

1.1.2.1 Glass transition

A glass whose atomic arrangement lacks regularity over a long range generally has higher configuration entropy, and hence higher free energy, than a crystalline material of the same composition. In other words, a glass is a thermodynamically metastable material which remains un-transformed to its most stable state due to hindrance of the atomic rearrangement during the process of glass formation. The transformation of a glass to a crystal proceeds via nucleation and crystal growth under the driving force of the difference in free energy between crystal and glass, ΔG_v , which increases with the increase of super cooling ΔT_r . Both nucleation rate I_0 and crystal growth rate U are dependent on the viscosity η of a super-cooled liquid as well as on ΔG_v .

Since the viscosity η increases exponentially with decreasing temperature as shown in Fig. 1.4 [7], the influence of viscosity on the hindrance of atomic rearrangement increases with decreasing temperature, whereas the driving force for the transformation into crystal increases with decreasing temperature.

Thus the nucleation rate I_0 and crystal growth rate U are approximately expressed by the following Eq. (1.2) and (1.3) [8, 9]:

$$I_0 = k_1/\eta \exp(-g\alpha^3\beta/T_r(\Delta T_r)^2) \quad (1.2)$$

where k_1 is a constant (typically about 10^{30} dyne cm), $T_r = T/T_m$, $\Delta T_r = (T_m - T)/T_m$, g is a factor related to the shape of the nucleus and equal to $16\pi/3$ for a spherical nucleus, and α and β are dimensionless parameters given by

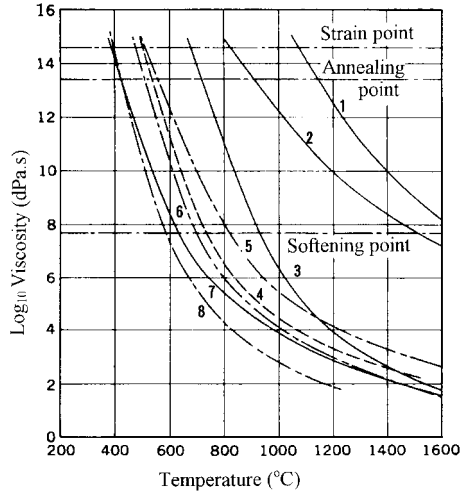


Fig. 1.4. Viscosity–temperature relationship of some commercial glasses. 1: Silicate glass; 2: High (96%) silica glass; 3: Aluminosilicate glass; 4: Soda-lime silicate glass (sheet glass); 5: Borosilicate glass; 6: Soda-lime silicate glass (electric bulb); 7: Lead-alkali silicate glass (electric use); 8: Lead-alkali silicate glass (high lead content). [7] [Reprinted from E. B. Shand, *Glass Engineering Handbook*, (McGraw-Hill Book Company, Inc., 1958) p. 16 copyright (1958) with permission from Corning Inc.]

$$\alpha = (N_A V_C^2)^{1/3} \sigma / \Delta H_{fM} \quad (1.2a)$$

and

$$\begin{aligned} \beta &= \Delta H_{fM} / RT_m \\ &= \Delta S_{fM} / R \end{aligned} \quad (1.2b)$$

where N_A is Avogadro's number, V_C is the molar volume of the crystal, σ is the crystal–liquid interface energy, ΔH_{fM} is the molar enthalpy of fusion and ΔS_{fM} is the molar entropy of fusion. For typical nonmetals, $\alpha\beta^{1/3}$ is about $0.5 \sim 0.7$.

$$U = f(RT/3N_A\pi\lambda^2\eta)(1 - \exp[\Delta H_{fM}\Delta T/RTT_m]) \quad (1.3)$$

where f is the fraction of the site at which the glass-to-crystal transition can take place on the crystal surface and $\Delta T = T_m - T$, respectively.

In the temperature range near melting point T_m , the influence of $\Delta H_{fM}/T_m$ is predominant and, in the temperature range well below melting point, the influence of viscosity η is very large compared with the influence of $\Delta H_{fM}/T_m$. The schematic illustration of I_0 and U as a function of temperature gives curves which pass through maximum as shown in Fig. 1.5.

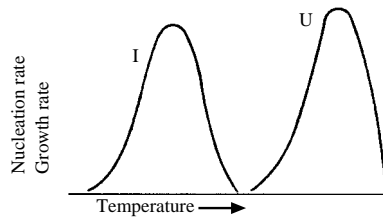


Fig. 1.5. Schematic illustration of temperature dependence of nucleation rate and crystal growth rate in a super-cooled liquid.

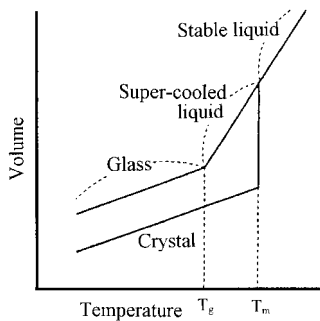


Fig. 1.6. Volume-temperature relationship of glass-forming liquid, and nonglass-forming liquid.

An important fact to be noted in the figure is that the temperature giving the maximum crystal growth rate (U) is higher than the one giving the maximum nucleation rate (I). When a viscous liquid is cooled from a high temperature, it passes through the temperature region of high crystal growth rate before nucleation takes place. When it passes through the temperature region of high nucleation rate, the crystal growth rate is already very low. Thus, a viscous liquid cooled at a sufficient rate further increases its viscosity to near or above 10^{14} dPa s without being transformed into a crystal. Once the viscosity reaches this value, even the alteration of the local atomic arrangement to equilibrate with temperature is not possible, resulting in the 'frozen-in' structure. Then the material behaves as a rigid and brittle solid, i.e. a glass. Physical and chemical phenomena occurring in a solid glass are no longer so sensitive to temperature change except for those that are enhanced by thermal activation such as the movement of alkali ions. Figure 1.6 shows the temperature dependence of the molar volume of a viscous super-cooled liquid, and uses glass as an example.

The transition from a viscous liquid to a solid glass is called the 'glass

transition' and the temperature corresponding to this transition is called the 'glass transition temperature', T_g . The reversible transformation from a glass to a viscous liquid also takes place if a glass is heated to a temperature above T_g .

Since the glass transition occurs as a result of the increase of viscosity and the rate of viscosity increase is dependent on cooling rate, the glass transition temperature, T_g , is not always the same even if the chemical composition is the same, but instead it is usually different, depending on the cooling rate of a liquid. A slow cooling allows enough time for a viscous liquid to alter its local atomic arrangement to attain the minimum free energy at the corresponding temperature, whereas a rapid cooling causes an increase of viscosity that is too quick for the local atomic arrangement to follow and results in a transition into a glass at a higher temperature.

The structure of a rapidly cooled glass is more open than that of a slowly cooled one because the 'freezing-in' of the atomic arrangement occurs at a higher temperature. The properties of a glass are therefore different from glass to glass, depending on the thermal history, even if the chemical composition is the same.

1.1.2.2 Thermal stability and structural relaxation

A glass obtained by cooling a liquid can transform into a crystal if re-heated to a temperature region that is well above T_g , where the nucleation and crystal growth takes place. Figure 1.7 shows an example of the crystallization of a glass detected by a differential thermal analysis (DTA) [10]. The exothermic peak observed in the temperature near 700 °C is attributed to crystallization. The sharpness of the peak and the difference between onset temperature and T_g reflect the thermal stability of a glass. If a glass is thermally unstable, the exothermic peak is sharp and the temperature difference is small.

On the other hand, if the temperature of re-heating is not high and remains near the glass transition temperature, which is well below the temperature giving high crystal growth rate, a glass remains uncrystallized but undergoes some change in atomic arrangement called structural relaxation [11]. The differences in structure and properties between glasses of different thermal history can be eliminated by the structural relaxation brought about by this heat treatment near the glass transition temperature. Figure 1.8 shows an example of such a change attributed to the structural relaxation [12]. It should be noted from this figure that the tuning of some properties of glass is possible by holding the glass at a temperature near the transition temperature.

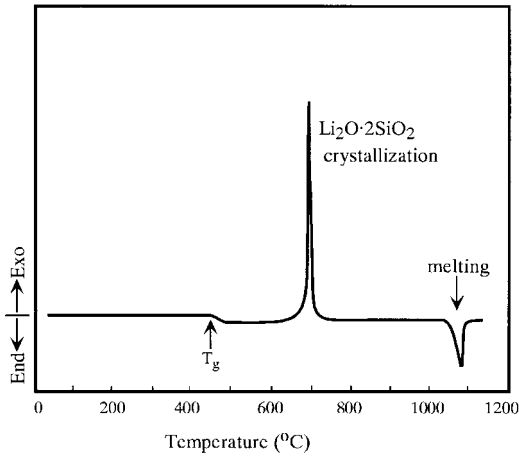


Fig. 1.7. Differential thermal analysis curve of $\text{Li}_2\text{O}-\text{SiO}_2$ glass heated at a rate of $10^\circ\text{C min}^{-1}$ [10].

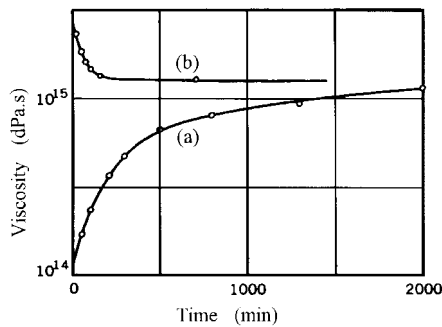


Fig. 1.8. Viscosity–time curves of a soda-lime silica glass at 486.7°C [12]. (a) Newly drawn fiber; (b) Fiber stabilized at 477.8°C for 64 h.

1.1.3 Optical features

1.1.3.1 Transparency

There is neither grain boundary nor interface within a glass structure and so the intrinsic scattering loss of a glass is very small. Therefore, a glass is, in principle, transparent to light in the wavelength region where the intrinsic absorption does not occur, i.e. between two intrinsic absorption edges determined by band-gap energy and the vibration energy of constituents.

Glasses of oxide and fluoride systems that have a wide gap between the conduction and valence bands are generally transparent to light in the visible

and near infrared region, whereas those of the chalcogenide system have narrower band gaps and are generally translucent in the visible region but transparent in the near infrared and infrared regions as shown in Fig. 1.9 [13].

Owing to its high transparency to visible light, glass has long been used as the key material for various optical components. Taking advantage of the flexibility of composition, over two hundred kinds of commercial optical glasses have been developed to date.

The primary requisite for an optical glass are high purity and high homogeneity to allow the propagation of a light beam with minimum optical loss. The optical loss inherent to a glass of given composition consists of: (a) intrinsic absorption loss due to the transition of electrons from the valence band to the conduction band which is determined by the band gap energy between two bands; (b) absorption loss due to vibration of molecules; and (c) loss due to Rayleigh scattering. The values of these losses vary with the wavelength of light according to Eqs (1.4), (1.5) and (1.6), respectively [14–16];

$$\alpha(E)_{\text{uv}} = \alpha_0 \exp[A_0(E - E_g)/kT] \quad (1.4)$$

where E is phonon energy, $\alpha(E)_{\text{uv}}$ is the absorption coefficient at photon energy E , due to intrinsic absorption loss in UV region, E_g is band gap energy between the valence band and conduction band, k is Boltzmann constant, and α_0 and A_0 are constants [14].

$$\alpha(E)_{\text{IR}} = \alpha_2 \exp(-E/E_2) \quad (1.5)$$

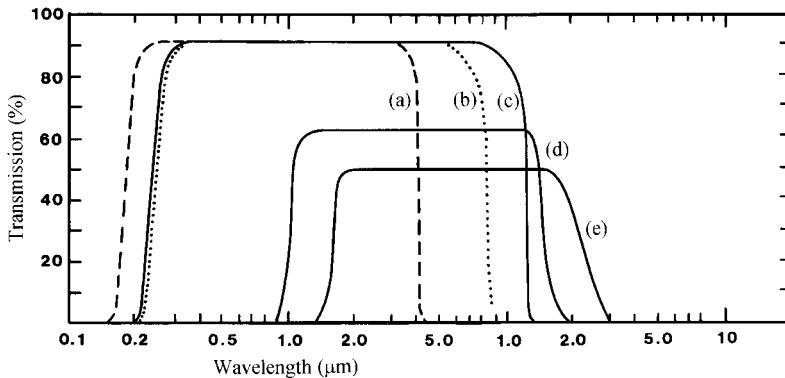


Fig. 1.9. Optical transmission curves of representative oxide, fluoride and chalcogenide glasses. (a) Silica glass, (b) 57HfF₄-36BaF₂-3LaF₃-4AlF₃ (mol%) glass; (c) 19BaF₂-27ZnF₂-27LuF₃-27ThF₄ (mol%) glass; (d) As₂Se₃ glass; (e) 10Ge-50As-40Te (atom%) glass. [Reprinted from M. G. Drexage, *Treatise on Materials Science and Technology*, Vol. 26, Glass IV (Academic Press, Inc., 1985) p. 151, copyright (1985) with permission from Academic Press, Inc.]

where, $\alpha(E)_{\text{IR}}$ is the absorption coefficient at photon energy E due to vibration of molecules, and α_2 and E_2 are constants [15].

$$I_{\text{RS}}(\lambda) = (8\pi^3/3\lambda^4)[(\partial n^2/\partial \rho)^2(\delta \rho)^2 + \Sigma(\partial n^2/\partial C_i)^2(\delta C_i)^2]\delta V \quad (1.6a)$$

where

$$(\delta \rho)^2/\rho^2 = (\beta_c/\delta V)kT_F \quad (1.6b)$$

$$(\delta C_i)^2 = kT_F/(N_i\partial \mu_c/\partial C_i) \quad (1.6c)$$

and $\delta \rho$ is density fluctuation, δC_i is compositional fluctuation of the i th component, β_c is isothermal compressibility, T_F is the fictive temperature, k is Boltzmann constant, N_i is number of molecules of i th component contained in the unit volume of glass, μ_c is the chemical potential, and n is the refractive index of glass respectively [16].

Figure 1.10 depicts the change of respective losses with wavelength of light in the case of silica glass [17]. It is well known that the theoretical minimum loss is determined by the absorption loss due to vibration of molecules and Rayleigh scattering, and is about 0.125 dB km^{-1} in the vicinity of $1.55 \mu\text{m}$.

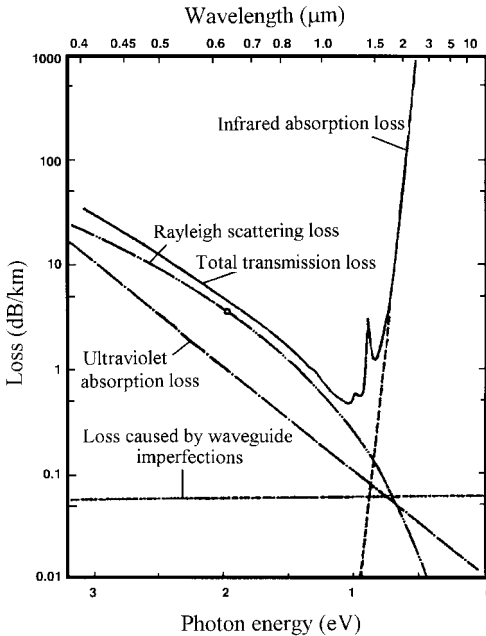


Fig. 1.10. Changes of intrinsic optical losses of P_2O_5 -doped SiO_2 glass with wavelength of light. [Reprinted from T. Miya, T. Terunuma, T. Hosaka and T. Miyashita, *Electron. Lett.* **15** (1979) 106, copyright (1979) with permission from the Institute of Electronic Engineers.]

It should be noted that the wavelength giving the minimum intrinsic loss is different from glass to glass depending on the type and amount of the constituents. The loss value of a practical glass is the sum of this intrinsic loss and the extrinsic loss attributed to the absorption by impure atoms and the scattering loss due to compositional heterogeneity, etc. Major impurities that cause absorption loss are transition metal ions and water. Absorption by transition metal ions is attributed to the transition of electrons between the d-orbital of two different energy levels determined by the influence of the ligand of the ion. The absorption spectra assigned to various transition metals in a silica glass are shown in Fig. 1.11 as examples [18].

The absorption loss due to water in a glass is attributed to the stretching vibration of the OH group and its coupling with the vibration of the metal–oxygen bond. The wavelength and intensity of such absorption in silica glass are shown in Table 1.1 as an example [19].

1.1.3.2 Linear and non-linear refractive index, and dispersion

Refractive index is another important property to be considered with respect to the optical features of glass. It is correlated with the electric dipole moment induced by the electromagnetic interaction of constituent atoms and molecules with light, and is expressed by Eq. (1.7) which is known as the Lorentz–Lorenz equation as [20]:

$$\begin{aligned} (n^2 - 1)V/(n^2 + 2) &= (4\pi/3)N_A\alpha \\ &= R \end{aligned} \quad (1.7)$$

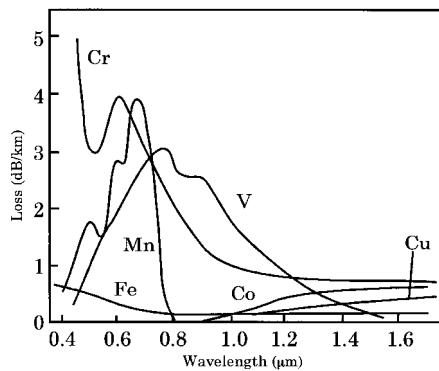


Fig. 1.11. Absorption spectra of various transition metal ions in a silica glass. [Reprinted from P. C. Shultz, *J. Am. Ceram. Soc.* **57** (1974) 309, with permission of The American Ceramic Society, Post Office Box 6136, Westerville, Ohio 43086-6136, copyright (1974) by The American Ceramic Society. All rights reserved.]

Table 1.1. Absorptions assigned to vibration of OH and their coupling with vibration of metal-oxygen bonds [Reprinted from P. Kaiser, A. R. Tynes, H. W. Astle, A. D. Pearson, W. G. French, R. E. Jeagar et al., *J. Opt. Soc. Am.* **63** (1973) 1141, copyright (1973) with permission from the Optical Society of America]

Wavelength λ (μm)	Vibration mode	Absorption loss (dB/km/ppm of OH)
2.73	ν_3	8300
2.22	$\nu_1 + \nu_3$	220
1.93	$2\nu + \nu_3$	8.6
1.39	$2\nu_3$	54
1.24	$\nu_1 + 2\nu_3$	2.3
1.13	$2\nu_1 + 2\nu_3$	0.92
0.945	$3\nu_3$	0.83
0.88	$\nu_1 + 3\nu_3$	7.5×10^{-2}
0.82	$2\nu_1 + 3\nu_3$	3.3×10^{-3}
0.72	$4\nu_3$	5.8×10^{-2}
0.68	$\nu_1 + 4\nu_3$	3.3×10^{-3}
0.64	$2\nu_1 + 4\nu_3$	8.3×10^{-4}
0.60	$5\nu_3$	5.0×10^{-3}

ν_3 , Stretching vibration of Si-OH;
 ν_1 , Stretching vibration of Si-O.

where V is molar volume, n is refractive index, α is polarizability, N_A is Avogadro's number, and R is molar refraction.

When the number of vibrating electrons in the presence of an electric field E , which changes periodically with frequency ω , is large, the polarizability α is expressed as:

$$\alpha = (e^2/4\pi^2 m)\Sigma[f_i/(\omega_i^2 - \omega^2)] \quad (1.7a)$$

where e is charge of an electron, m is mass of electron, ω_i is the frequency of vibration of an electron in the i th ion, and f_i is the oscillator strength of the intrinsic absorption of the i th oxygen ion, respectively. The refractive index of a glass is then written as:

$$(n^2 - 1)/(n^2 + 2) = N_A(e^2/3\pi m)\Sigma[f_i/(\omega_i^2 - \omega^2)]. \quad (1.7b)$$

The values of ω_i of a material which are non-absorbing in the visible region of the spectrum lie within the range of the shorter wavelengths and $\omega_i > \omega$. The refractive index n of a glass given by this equation is in the range 1.45 to 2.00 depending on the composition of the glass and decreases gradually with the

increase of wavelength of light in the visible region, as shown in Fig. 1.12 [21]. This dependence of refractive index on wavelength of light is called dispersion and is also an important parameter used to describe the optical properties of a glass.

The dispersion of a glass is usually represented either by 'average dispersion' $n_F - n_C$ or by the Abbe number ν_d given by Eq. (1.8).

$$\nu_d = (n_d - 1)/(n_F - n_C) \quad (1.8)$$

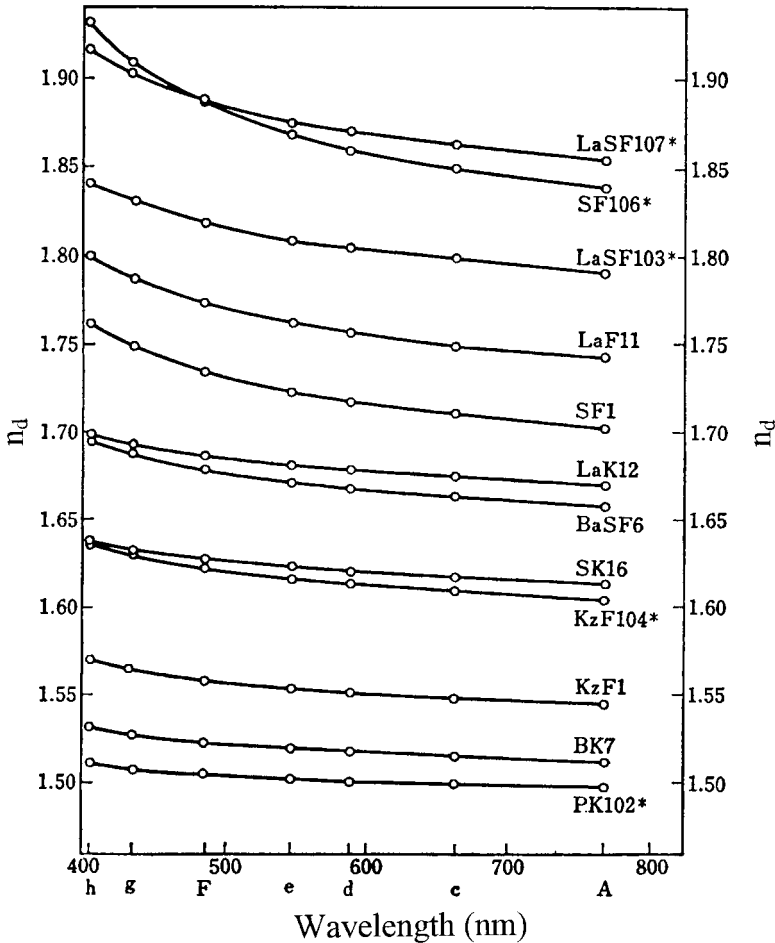


Fig. 1.12. Some examples of the change of refractive index of optical glasses with wavelength of light [21].

where n_d , n_F , n_C are the refractive indices for the d-line of He (wavelength: 587.56 nm), the F-line of H (wavelength 486.13 nm) and the C-line of H (wavelength 656.27 nm), respectively.

The relations described above, or the refractive index of ordinary optical glasses used for lenses, prisms, etc., apply within the range where the linear relationship, given by Eq. (1.9), holds between the polarization P and electric field E .

$$P = \chi^{(1)}E \quad (1.9)$$

where the proportionality coefficient $\chi^{(1)}$ is called linear susceptibility. Under high electric fields such as those caused by the irradiation of strong coherent light such as laser beams, however, the induced polarization does not change linearly with applied field but increases nonlinearly as expressed by Eq. (1.10) [22]

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots \quad (1.10)$$

where, the coefficients $\chi^{(2)}$ and $\chi^{(3)}$ are called second- and third-order nonlinear susceptibilities, respectively.

In an isotropic material like glass, the second-order nonlinear susceptibility $\chi^{(2)}$ becomes zero and the nonlinearity at orders higher than four is negligibly small. The Eq. (1.10) is rewritten as Eq. (1.10') for an ordinary glass

$$P = \chi^{(1)}E + \chi^{(3)}E^3. \quad (1.10')$$

Consequently, the refractive index of a glass n also varies with the intensity I of light as:

$$n = n_0 + (12\pi\chi^{(3)}/n_0)E^2 = n_0 + n_2''I \quad (1.11)$$

where n_0 is the linear refractive index when the relation in Eq. (1.9) holds, and n_2'' is the nonlinear refractive index. Application of this nonlinear effect is one of the key technologies in the field of optics and optoelectronics and will be reviewed in Chapter 4.

1.2 Classification of glasses by preparation method

1.2.1 Glass by melt-quenching technique

Before the development of the chemical vapor deposition and sol-gel processes, the melt-quenching technique was the only method by which bulk glasses of acceptable size for practical application could be obtained. Even today, glasses produced by the melt-quenching technique make up more than 99% of practical glasses in both volume and number of types. The process, which is based on the fusion of crystalline raw materials into a viscous liquid

followed by forming it into a shape and quenching to a glass [23], is distinguished from other methods of glass preparation in many aspects including the available systems, size and shape of the products, number of components, etc.

A batch mixture prepared by mixing predetermined amounts of pulverized crystalline raw materials to attain the desired property is placed in a tank furnace made of firebrick or into a crucible made of clay, platinum, etc. to be fused into a liquid at high temperature. A tank furnace is designed to allow the continuous mass production at a daily pull of 40 ~ 600 tons of glass by charging the batch mixture from one end and taking the molten glass out of the other end of the furnace to feed to a forming machine.

When glass which has a special property is required in a limited amount, the melting of a batch mixture is made using a crucible with an externally supplied heat source such as the combustion of fossil fuel or electricity using an induction coil, and then supplied to a forming machine. Depending on the application, the melt is sometimes cooled very slowly to a rigid condition within a clay crucible so that only the highly homogeneous part is used. Generally the molten glass is kept at the temperature which corresponds to a viscosity of $10 \sim 10^2$ dPa s, i.e. 1400 ~ 1500 °C for most commercial glasses as shown in Fig. 1.4, for more than 10 h in order to remove tiny bubbles and to enhance the homogenization of the melt through convection and the inter-diffusion of the constituent atoms.

The formation of a melt into a desired shape is carried out at a temperature corresponding to the viscosity of $10^3 \sim 10^4$ dPa s, i.e. 900 ~ 1100 °C for most commercial glasses, by applying various forming methods such as casting into a mold, blowing, up-drawing, down-drawing, pressing, rolling out, floating, and various combinations, and in this way the high flexibility in the geometry of products, which is the most distinctive feature of the melt-quenching technique, is possible. It is well known that a continuous glass ribbon of about 5 m wide and 0.5 ~ 20 mm in thickness is routinely produced in the sheet glass industry throughout the world; a continuous glass fiber of several microns in diameter is drawn through a platinum nozzle; and an optical glass for telescope lens of the diameter exceeding 1 m is easily obtainable.

Most of the formed glasses are usually annealed in a temperature range that is slightly higher than the glass transition temperature (shown as the annealing point in Fig. 1.4) to remove any thermal stress which developed during the forming and subsequent cooling due to the low thermal conductivity of a glass.

The additional feature of the melt-quenching method, namely the high flexibility of the geometry of a glass and particularly the advantage in obtaining materials of large size in comparison with a single crystal or polycrystalline ceramics, is as important as the structural and thermodynamic features when

Table 1.2. Chemical composition of some industrial glasses manufactured by melt-quenching technique (wt%) [24]

Glass	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	PbO	Other
Sheet glass by float	72.6	1.8	–	7.9	3.8	12.2	–	–	0.7
Container glass	72.8	1.6	–	11.3	–	13.8	–	–	0.5
Crystal glass	56.9	–	–	–	–	2.8	13.6	26.0	0.3
Optical glass SF6	26.9	–	–	–	–	0.5	1.0	71.3	0.3
Optical glass BK7	66	–	12.4	–	–	8	12	–	1.6
Laboratory ware	80	2.25	13	–	–	3.5	1.15	–	0.9
Electric glass (stem)	57	1	–	–	–	3.5	9	29	0.5
TV panel glass	63.8	1.3	9.4 (SrO)	2.9	2.2 (BaO)	7.2	8.8	2.8	1.6
TV funnel	51	4	–	8 ^a	–	6	7.5	23	0.5
TV neck	47	3.3	–	3.4 ^a	–	3	10	33	0.3

^aRO (= CaO + BaO + SrO).

considering the preparation of glasses with special properties. Good examples of the products based on this feature are the giant pulse laser, Faraday rotator, etc., whose total performance is dependent on the size of material.

The other advantage of the melt-quenching technique over chemical vapor deposition or the sol-gel process is the large flexibility of composition. Since simple quenching of a melt does not require stoichiometry among constituents, the preparation of glasses with a wide variety of compositions, consisting of sometimes up to ten kinds of constituents at various ratios from a few to several tens of percent, is possible. The doping or co-doping of active ions such as rare-earth or transition metal at a level of a few percent or less is also made relatively easily, which is quite important for the production of glasses with special properties. As shown in Table 1.2, most of the important industrial glasses are based on this advantage of flexibility of composition. Examples of the glasses are color filters, and various glass lasers, etc.

The important fact that should be stressed about the melt-quenching technique is that most of the above-mentioned features are true not only for the familiar silicate, borate, or phosphate systems but also for the many exotic glasses of the oxide system as well as non-oxide glasses such as those of the fluoride and metal alloy systems. It should, however, be noted that there are some disadvantages in the melt-quenching technique compared with other processes. The melt-quenching technique which uses pulverized crystalline raw materials has disadvantages for the preparation of glasses of ultra-high purity such as those used for optical communication in comparison with the chemical vapor deposition and sol-gel processes that use liquid raw materials. The

Table 1.3. *Examples of metal halides and their boiling points employed in glass formation by chemical vapor deposition process [27]*

Formula	Melting point (°C)	Boiling point (°C)	Density (g cm ⁻³)
SiH ₃ Cl	-118	-30.4	1.15
SiH ₂ Cl ₂	-122	8.3	1.42
SiHCl ₃	-127	31.8	1.35
SiCl ₄	-70	57.6	1.48
GeCl ₄	-49.5	84.6	1.84
PCl ₃	-93.6	74.7	1.57
POCl ₃	1.3	105.1	-
BBr ₃	-46.0	96.0	-
AlBr ₃	97.5	263.3	-
TiCl ₄	-25	136.4	1.726

difficulty of maintaining high purity is also attributed to possible contamination by the crucible or furnace materials which often react with the glass melt under high temperature. In order to minimize the contamination, crucibles made of noble metal such as platinum and its alloys are often used for the preparation of special glasses.

Another disadvantage of the melt-quenching technique that should be noted is that it is extremely difficult to prepare glasses containing a large amount of refractory material represented by SiO₂, TiO₂, Al₂O₃, ZrO₂ etc. by this technique because of the requirement for an extremely high temperature for melting. The production of the binary or ternary glasses containing these components, as well as silica glass of ultra-high purity, are therefore made by either chemical vapor deposition or the sol-gel process.

1.2.2 Glass by chemical vapor deposition

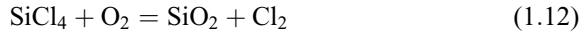
The preparation of a bulk glass by the chemical vapor deposition (CVD) method was developed in the early 1940s [25]. The process is based on the thermally activated homogeneous oxidation or hydrolysis of the initial metal halide vapor (or mixture of metal halides) to form particulate glass material 'soot', followed by viscous sintering of the soot into solid inclusion-free glass bodies [26]. Examples of the metal halides employed in this process are shown in Table 1.3 along with their melting and boiling points [27].

The oxidation or hydrolysis reaction is usually activated by either oxygen plasma or an oxy-hydrogen flame. In the case of the formation of silica glass

Table 1.4. *Melting point and boiling point of chlorides of transition metals, rare-earth elements and some alkali and alkaline earth metals [27]*

Formula	Melting point (°C)	Boiling point (°C)
FeCl ₃	300	317
CuCl ₂	422	1366
CrCl ₃	1150	–
NiCl ₃	1001	–
MnCl ₃	650	1190
CoCl ₃	500	1049
EuCl ₂	727	>2000
ErCl ₃ ·6H ₂ O	774	1500
NdCl ₃	784	1600
SmCl ₃	678	–
LiCl	605	1325–1360
NaCl	801	1413
CaCl ₂	782	>1600
BaCl ₂	963	1560

from SiCl₄, the reaction is schematically shown by Eq. (1.12) and (1.13), respectively



The typical reaction temperature in the former case is about 2000 °C, whereas the sintering temperature of the soot into a glass is about 1800 °C [28]. The most distinctive difference between the reaction using oxygen plasma and that using an oxy-hydrogen flame is the level of OH contained in the eventual glass. The hydroxyl level in the silica glass produced by using oxygen plasma is as low as 1 ppm OH, whereas the typical hydroxyl level in a silica glass by the latter method is 1000 ppm OH.

The feature of this method is that the initial metal halides are liquid at or in the vicinity of room temperature and their boiling points are very low compared with the boiling points of the halides of alkali, alkaline earth, transition metals, or rare-earth elements, examples of which are shown in Table 1.4 [27]. This means that the purification of raw materials is easily made by repeating the distillation at a temperature well below the melting points of the halides in this table.

Thus, the process has many advantages over the melt-quenching technique for preparing glasses of ultra high purity, particularly the preparation of glasses

that are free from transition metal elements. In addition, it is possible to prepare glasses whose chemical composition can be varied continuously or step-wise by changing the mixing ratio of the raw materials. The method, however, is not suitable for the preparation of glasses containing alkali and alkaline earth elements or for glasses doped with rare-earth elements.

The types of special glasses that are produced by using the advantage of this process include high-purity silica glass used for various optical and opto-electronic devices [26], $\text{TiO}_2\text{-SiO}_2$ glass of ultra-low thermal expansion used for the mirror blanks for telescopes [29], the preforms of optical fiber for telecommunications [30] etc.

An optical fiber produced by the chemical vapor deposition process is 125 μm in diameter and has a core-clad structure as shown in Fig. 1.13. The refractive index of the core is slightly (0.1 ~ 0.3% and 0.8 ~ 2% depending on the type of the fiber) higher than that of the cladding. The optical signal enters the fiber and is propagated within the core along the fiber axis. The fiber is classified into three types depending on the refractive index profile of the core-clad structure which determines the mode of propagation of the optical signal.

The single mode fiber whose core diameter is 8 ~ 10 μm allows the

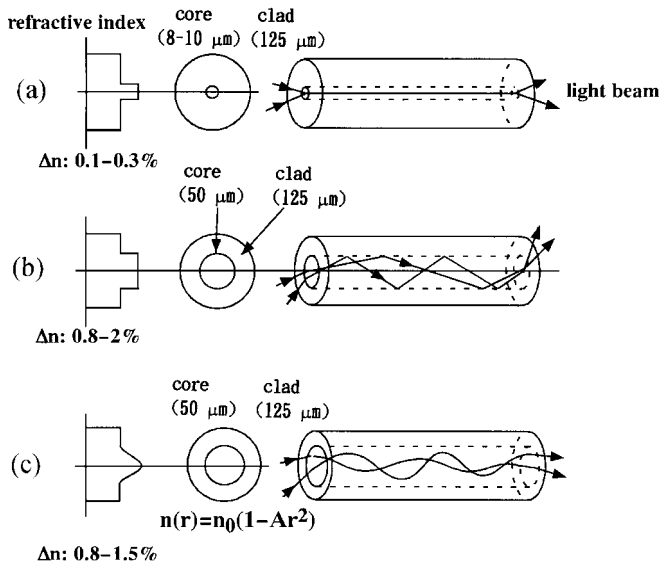


Fig. 1.13. Structure of optical fiber for telecommunications. (a) Single-mode fiber. (b) Multi-mode fiber of step index type. (c) Multi-mode fiber of graded index type.