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Intrinsic Loss
in Infrared Optical Fibers

by

Prapassorn Tantiphanwadi

A report in partial fulfillment
of the requirements for the degree of

MASTER OF SCIENCE

in

Physics

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I INTRODUCTION

Recently, in communication system, fiber optics has become a most interesting development tool as a transmission medium. It first appeared as a feasible transmission medium in 1970. The reason for the development in fiber optics comes from the overwhelming advantage in technology and economy compared to wires and coaxial links. For technology progress, typically, optical fiber has a wide transmission band-width (0.1-1000 GHz), lower loss per unit length ($0.15 - 5 \text{ dB km}^{-1}$ [1]), and does not allow electromagnetic interference. For example, signal transmitted over commercial silica-based fiber must be reamplified every 10 to 50 kilometers, whereas signals transmitted over copper wires must be reamplified every 4 to 6 kilometers. The economical advantage are as follows: a typical cable fiber weighs only about 3 kg/km; costs under \$500/km or less, and has a longer repeater spacing of up to 100 km or more at a data rate of at least several hundred megabits per second. Because the optical fibers meet both demands, it has enabled us to construct high bit-rate and long haul communication systems in metropolitan area.

The type of optical fiber which has major impact on today well-developed technology is the silica-based fiber. Widespread use of the fiber is in communications, medicine, industry, military, etc. It can transmit in the wavelength approximately to $3 \mu\text{m}$ and has achieved an intrinsic loss of 0.2 dB km^{-1} at $1.5 \mu\text{m}$ [2]. In many IR electro-optical systems, there are needs to transmit in wavelengths which require entirely different materials and fabrications. This has encouraged many researchers to develop IR fiber optics because it can transmit longer wavelengths from 2 to $14 \mu\text{m}$ [2].

This report is divided into five chapters. Following this introductory chapter, basic concepts about IR optical fibers, intrinsic transmission loss, materials, and classification of optical fibers are described in chapter 2. Chapter 3 and chapter 4 are concerned about intrinsic transmission loss in glasses and crystals, respectively. Chapter 5 is a summary of the distinct properties of each kind of IR optical fibers.

II INTRODUCTION TO IR OPTICAL FIBERS

In 1979, IR fibers, the second generation following to silica-based fiber, has emerged by its promising wider transparencies in wavelengths than those of silica-based fibers. The distinctive discussions about the possibility of ultralow loss less than 0.02 dB km^{-1} for IR transmitting materials are made by Pinnow *et al.* [3], Van Uitert and Wemple [4], and Goodmand [5]. These discussions motivated investigations of nonsilica-based IR fiber materials. In this chapter, IR transmission loss, materials and classification of the optical fibers are described.

A. Loss mechanisms in IR optical fibers

1. General description of transmission loss

When light travels through a medium, its intensity gradually decreases with distance because of its interaction with the constituent atoms, such as absorptions and scatterings. The intensity I of the light transmitted in the material of thickness z along the direction of propagation is expressed as

$$\frac{I}{I_0} = \exp(-\alpha z) \quad (2.1)$$

where I_0 is the intensity of the input light and α is the absorption coefficient.

The loss of power in the fiber through absorption, scattering, etc., is referred to as its attenuation and is expressed in terms of loss per unit of length by the formula

$$\text{Attenuation} = -\left(\frac{10}{L}\right) \log_{10} \left(\frac{\text{Power out}}{\text{Power in}} \right) \quad (2.2)$$

where L and the attenuation are expressed in kilometers and units of decibels per kilometer (dB

2. The transmission loss mechanism

The transmission loss of optical fiber can be divided into two groups, intrinsic and extrinsic losses. All of the losses are listed in table 2.1 and are shown in Fig.2.1.

Table 2.1 Loss factors of optical fiber [13].

Intrinsic loss	Intrinsic absorption loss	<ul style="list-style-type: none"> Loss due to electronic transition Loss due to lattice vibration
	Intrinsic scattering loss	<ul style="list-style-type: none"> Rayleigh scattering Raman scattering, etc.
Extrinsic loss	Impurity absorption loss	<ul style="list-style-type: none"> Transition metal absorption Absorption due to OH vibration
	Scattering loss due to structural imperfection	<ul style="list-style-type: none"> Loss due to imperfection at the boundary between core and cladding Loss due to pores, etc. Loss due to microbend

2.1. loss factors

In this section, all of the loss factors in table 2.1 are determined as the sum of intrinsic and extrinsic factors and are expressed as the transmission loss α is given by

$$\alpha = \frac{A}{\lambda^4} + B + C \exp(D/\lambda) + E(\lambda) + F(\lambda). \quad (2.3)$$

The first factor of equation (2.3) is due to the intrinsic scattering loss which can be shown to depend on wavelength as A/λ^4 . The second factor is the scattering loss due to structural imperfections and does not depend on the wavelength. Therefore, it is only

represented by a constant, B . The third factor is the absorption due to electronic transitions and can be represented as $C \exp(D/\lambda)$, where λ is the wavelength, and C and D are the constants. The last two factors represent for the absorption due to lattice vibrations (phonons) and the impurity absorption as $E(\lambda)$ and $F(\lambda)$, respectively.

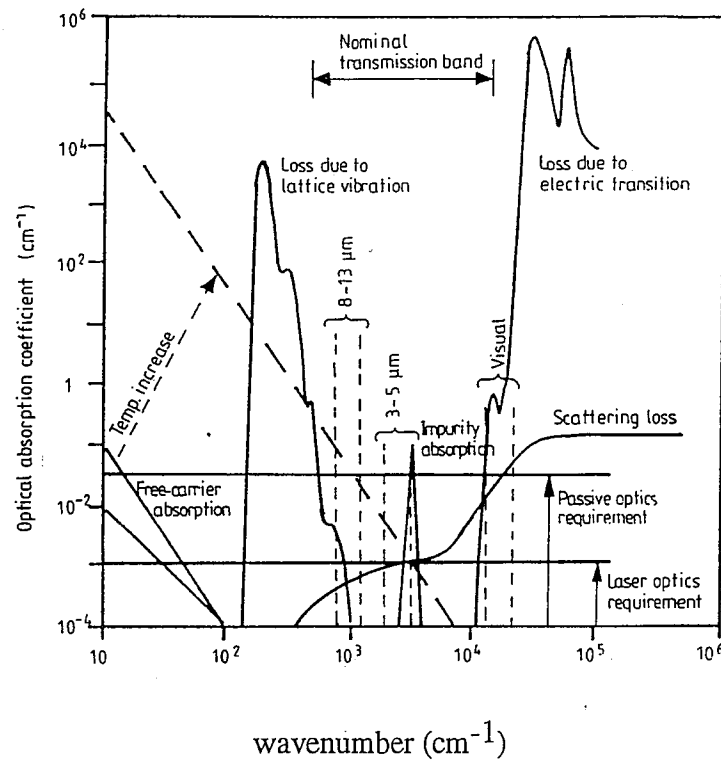


Fig. 2.1. Various losses of optical fibers [after T. Katsuyama].

2.2. Intrinsic absorption loss mechanisms in IR optical materials

In solids (semiconductors and insulators), there are two kinds of intrinsic absorption mechanisms which define their regions of transparency to IR radiation. In the first case, if the electromagnetic radiation has sufficient energy (short enough wavelength) to excite the valence electrons across the band gap to conduction band. This mechanism is called electronic transition. However, lower frequency electromagnetic radiation (longer wavelength) is absorbed by a different mechanism. This interaction occurs between radiation of mid to very far-IR wavelengths and the vibrational modes of the lattice of the materials.

Loss due to electronic transitions

Absorption mechanism can take place for the photon energies just below the energy gap, which is known as Urbach's rule [43]. This mechanism corresponds to the electron transition from the valence band to exciton levels. The observed exponential absorption edges can be expressed in the form

$$\alpha \propto \exp g (E - E_0), \quad \text{where } g = \frac{\sigma}{k_B T}, \quad (2.5)$$

k_B is Boltzmann's constant, T is the absolute temperature and α is the absorption coefficient.

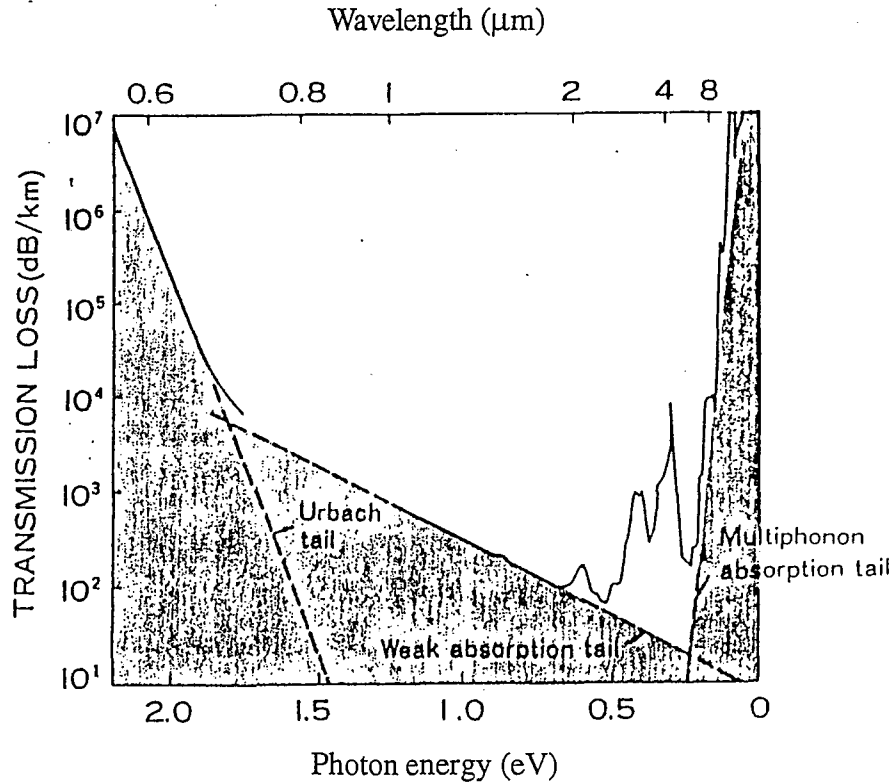


Fig.2.2. Transmission loss versus photon energy for As₄₀S₆₀ bulk glass and unclad fiber. This spectrum shows a typical Urbach, Weak absorption and Multiphonon absorption tail [after T. Izawa].

Weak absorption tail

At very low absorption region, where the absorption coefficient is smaller than 1 cm⁻¹,

temperature. Fortunately, in this case, there are theoretical models, both classical [7,8] and quantum mechanical [8,10,11] models exist, that accurately characterized the absorption loss. And the most acceptable model is based on the Morse interatomic potential. The potential leads to an exact solution of the Schrodinger equation and includes anharmonic effects to all orders.

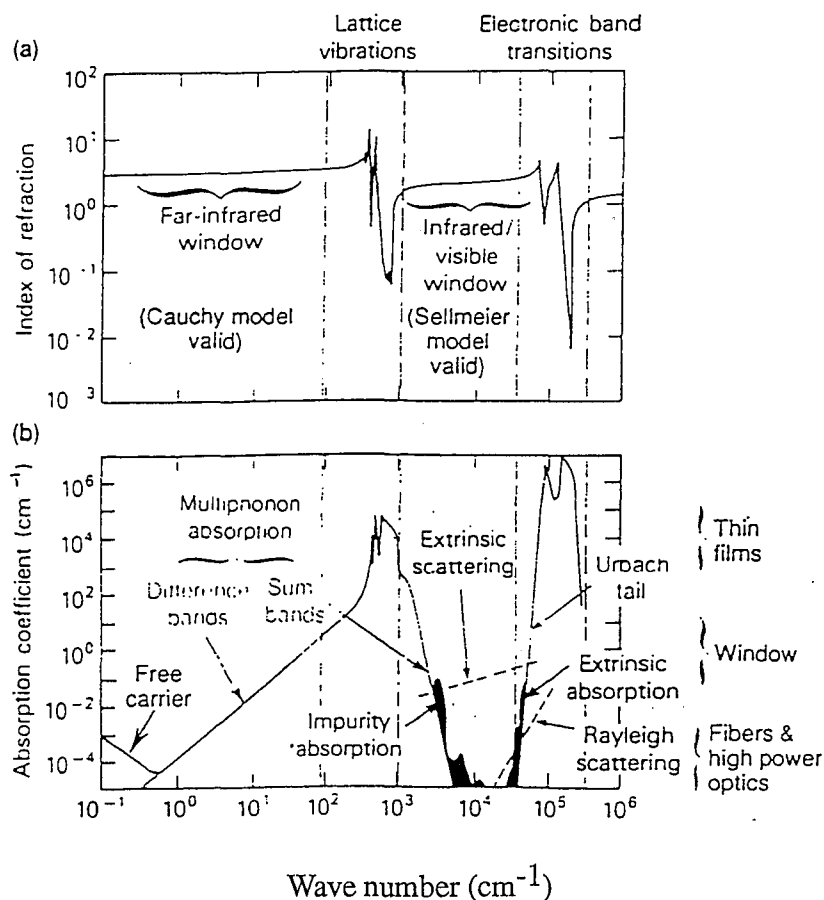


Fig.2.3. Optical properties of solids in terms of the complex index of refraction: (a) the index of refraction (real part) and (b) the absorption coefficient which is proportional to the imaginary part of the complex index of refraction [Michael E.].

Multiphonon absorption in homopolar and ionic crystals

In linear non-polar molecules (i.e. O_2 , N_2 , etc.), IR absorption cannot be expected because of no change in electric moment which is caused by molecular vibrations. However, because of induced dipole charges on the atoms, a second mode may bring electric moment of the second order which is caused by the vibration of the induced charges and so couple to the

electromagnetic light. The absorption coefficient for these second order effects are generally several orders smaller in magnitude than that of reststrahlen absorption.

Multiphonon absorption in ionic crystals is a form similar to that in homopolar crystals. Its strength is usually greater than in the homopolar case but still much weaker than the one phonon Reststrahlen absorption.

2.3. Intrinsic scattering loss

There are many kinds of scattering losses, Raman scattering, Brillouin scattering, Mie scattering, etc., but the most important loss is the Rayleigh scattering loss. Other scattering losses are relatively small. Rayleigh scattering is caused by the small particles or inclusions in the material. It can be shown that the angular intensity distribution of radiation scattering is of the form [17]

$$I(\theta) = \left(\frac{1 + \cos^2 \theta}{x^2} \right) \frac{8\pi^4}{\lambda^4} r^6 \left(\frac{N^2 - 1}{N^2 + 1} \right)^2 I_0, \quad (2.16)$$

where $I(\theta)$ is the specific intensity at the scattering angle θ ,

x is the distance from the scattering center,

r is the radius of the inclusion,

N is the ratio of refractive indices of inclusion is larger than that of the medium,

the scattering light intensity changes linearly with $[(N^2 - 1)/(N^2 + 1)]^2$ and r^6/λ^4 .

Equation (2.16) is a general formula which can be used for both crystals and glasses.

2.4 . Projected minimum intrinsic loss

The dominant sources of intrinsic loss are Rayleigh scattering and IR absorption (other intrinsic loss mechanisms are negligibly small). The location and value of the loss minimum can be estimated from the intersection between the Rayleigh scattering curve and the IR absorption edge as shown in Fig.2.4.

B. Materials for IR transmission

There are many requirements for optical fiber materials to use for fabricating high quality fibers. First, optical loss properties which is concerning about minimum intrinsic loss and the possibility of extrinsic loss reduction. Second, refractive-index control is for precise control of refractive index in radial direction and the reduction of index fluctuation along the axial direction. Third, shape control, the transmission characteristics of fibers can be strongly affected by cross sectional shape and size, the surface finish and the fluctuation of the size along axial direction of fibers.

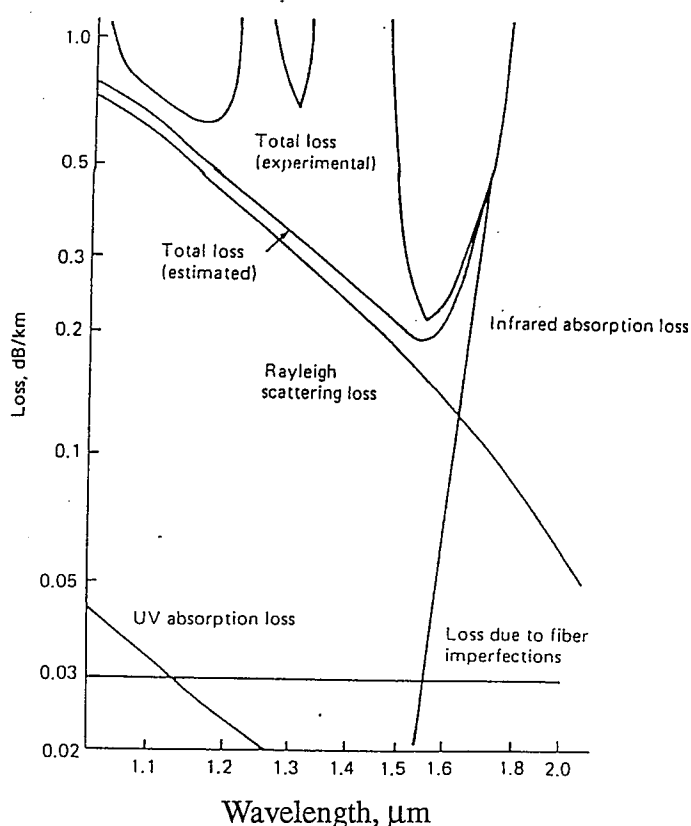


Fig.2.4. Components of optical loss in optical fibers [after T. Miya *et al*].

All of these three requirements are necessary for high quality fibers. In order to get high quality optical fibers, one must be concerned with what kinds of materials(gas, liquid, crystal or glass) meet most of those requirements.

In gases, optical losses are very low in the visible and near IR regions but because of the defect make their refractive index is difficult to control. Some liquid materials have low

loss properties suitable for low loss fibers. Their wide variety of refractive index can be chosen and this makes the waveguide characteristic of liquid is hard to maintain precisely.

The optical properties of solid state materials are much more stable than those of gases and liquids but their transmission losses are higher because of stronger interaction with electromagnetic wave. Strong absorptions occur at UV and IR wavelength regions. Solid-state materials are classified into two groups: crystalline state and amorphous state.

(i) Crystalline materials, such as quartz, sapphire, and alkaline halides, have essentially very low optical loss compared to amorphous materials. This is because Rayleigh scattering loss is less than one tenth of that of amorphous materials. Due to minimum intrinsic loss, single crystals can be the most suitable materials but high speed crystal growth and refractive-index control are difficult. Polycrystalline materials are usable even though their transmission loss is higher than expected from the intrinsic material.

(ii) Noncrystalline or amorphous materials, such as oxide glass, fluoride glass and chalcogenide glass are highly transparent in visible and IR wavelength regions. Rayleigh scattering loss due to density fluctuation is larger than that of crystalline materials but is much smaller than the loss caused by grain boundary scattering. These glasses are easily fabricated without introducing extrinsic scattering sources such as specific crystal surface roughness or grain boundaries. Moreover, the refractive indexes are easy to control without severely limiting the glass formation condition. For example, silica glasses, have high transparency in the visible and near-IR wavelength region and high chemical and mechanical durabilities. The refractive index can be changed easily by doping with other oxides such as GeO_2 , Al_2O_3 and TiO_2 . Moreover, the raw materials are relatively cheap. Therefore, silica glass is one of the most suitable materials for today low loss optical fibers in many respects.

In the following section, the fundamental characteristics of intrinsic loss, of the representative transparent materials in visible and near-infrared wavelength region (oxide glasses, fluoride glasses, chalcogenide glasses, single crystals and polycrystals) will be reviewed from the viewpoint of use as optical fiber materials.

1. Oxide glasses

The prototypical oxide glass is the amorphous form of silica. Its IR properties are

almost the same as those of crystalline SiO_2 , with a transparency region of 0.15 - 4.5 μm . In order to shift the IR absorption edge toward the longer wavelengths, glass composed of the elements with larger atomic numbers must be used. GeO_2 - and TeO_2 -based glasses are typical heavy-metal oxide glasses.

2. Halide glasses

BeF_2 , ZrF_4 , HfF_4 , and AlF_3 - BaF_2 are typical fluoride glasses. These fluoride glasses are promising materials for fiber use in the IR wavelength region even though they are not as stable against moisture when compared to oxide glasses. These glasses have very low-loss, compared to oxide glasses, in the wavelength region longer than 2 μm . BeF_2 glass has a transparency region 0.15 - 4.5 μm but is toxic and hygroscopic. Chloride glass, ZnCl_2 has a minimum loss of 0.001 dB km^{-1} in the 3.5 - 4 μm region [4], however it is too hygroscopic for practical use.

3. Chalcogenide glasses

For longer wavelengths IR transmission in the 3-11 μm region, a large family of glasses may be formed. Chalcogenide glasses are defined as glasses containing at least one of the elements S, Se and Te. As-S and Ge-S are typical chalcogenide glasses. Sulfide glasses have restricted IR absorption edges upto 10 μm ; on the other hand, selenide and telluride glasses have wider transparency regions, for example extending to 16 μm for Ge-As-Se.

4. Single crystals and polycrystals

Because of their low intrinsic transmission loss, single crystals are the ideal materials for low loss optical fibers. For alkali halide crystals, even though the intrinsic absorption loss is very small, they can not be obtained in the amorphous state. So, these materials must be used in crystalline state. However, the fabrication techniques of single crystal fibers have not been well developed.

Polycrystals have quite a great amount of grain boundary scattering loss. Halide polycrystals are a suitable choice since the fundamental phonon absorption bands are located in the far-IR and the optical transparency of these materials covers much broader spectral range than those of other materials.

C. Classification of IR optical fibers

As is discussed before, various kinds of IR materials have been investigated for fabricating suitable optical fibers. Optical fibers can be classified into two groups, dielectric and hollow optical fibers, which depended on how light propagates in the waveguides. The former waveguides can guide light in solid cores by total internal reflections, while the latter waveguides have core regions which are hollow. So the light guiding characteristics for each are different. In the following section, we will discuss only dielectric fibers which are categorized as glasses and crystalline fibers. The detailed classification of dielectric optical fibers is shown in table 2.2 [13], together with the minimum losses reported so far.

Table 2.2. Classification of dielectric IR optical fibers [13].

Classification		Typical example	Reported minimum loss (dB km ⁻¹)
Glass fiber	Oxide	GeO ₂ , GeO ₂ -Sb ₂ O ₃ and TeO ₂ -based glass fibers	4 (1.3 and 2 μm)
	Fluoride	ZrF ₄ -based and HfF ₄ -based glass fibers	0.7-0.9 (2-3 μm)
	Chalcogenide	As-S, Ge-S, As-Se, Ge-Se, Ge-As-Se, Ge-Sb-Se, and Ge-Se-Te glass fibers	35 (2.44 μm)
Crystalline fiber	Polycrystalline	TlBr-TlI (KRS-5) and AgCl fibers	70 (10.6 μm)
	Single crystalline	TlBr-TlI (KRS-5), AgBr, and CsBr fibers	300 (10.6 μm)

1. Glass fibers

1.1. Oxide glass fibers

IR oxide glass fibers are mainly based on heavy-metal oxides such as GeO_2 , $\text{GeO}_2\text{-O}_3$ and TeO_2 . The minimum losses typically occur at wavelengths of around 2-3 μm , and the theoretically predicted loss value is less than 0.1 dB km^{-1} . However, the best value reported is 4 dB km^{-1} ($\text{GeO}_2\text{-Sb}_2\text{O}_3$ glass fiber [15,16]) which is one order of magnitude larger than that of the conventional silica glass fiber.

One of the applications of these fibers is in ultra-low loss transmission lines for long distance optical communication. However, in order to realize such an application, further extensive studies are required, particularly to eliminate impurities.

1.2. Fluoride glass fibers

Typical materials for fluoride glass fibers are ZrF_4 - and HfF_4 -based glasses. These glasses exhibit a lesser tendency toward crystallization and higher IR transparency, compared to oxide and chalcogenide glasses. Theoretical prediction shows that fluoride glass fibers possess the lowest transmission losses of the IR optical glass fibers [26]. The minimum loss can be obtained at 2- 4 μm wavelengths. Losses as low as $0.7\text{ -}0.9 \text{ dB km}^{-1}$ at 2.5 μm have been reported [17,18]. Examples of these glasses are $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-LiF-PbF}_2$ and $\text{ZrF}_4\text{-BaF}_2\text{-GdF}_3\text{-AlF}_3\text{-PbF}_2$.

1.3. Chalcogenide glass fibers

Sulfide glass fibers can transmit light of wavelength 2 - 5 μm . The transmission loss has been reduced to less than 0.1 dB m^{-1} [18]. However, further loss reduction is thought to be difficult because of the existence of an intrinsic weak absorption tail. Since the sulfide glass fibers are thermally stable, they can be used of the short distance transmission in the fields of IR sensing systems, and laser surgery and machining.

On the other hand, selenide and telluride glass fibers have a wide transparency range, extended to 10 μm . However, the predicted minimum transmission losses, 1 dB m^{-1} [19], are higher than those of sulfide glass fibers. Therefore the main target of the research into these chalcogenide glass fibers is CO_2 laser power transmission at a 10.6 μm wavelength.

2. Crystalline fibers

2.1. Polycrystalline fibers

Typical materials so far are TlBr-TlI (KRS-5), AgCl , and AgCl-AgBr . In general, polycrystalline fibers show low losses in the wavelength region of more than 10 μm . The loss of as low as 0.1 dB m^{-1} at 10.6 μm [44] wavelength was achieved. Polycrystalline materials are characterized by a relatively low melting temperature and a high tensile strength. This fiber is useful for transmitting CO_2 laser power.

2.2. Single crystalline fibers

Materials for single crystalline fibers are almost the same as those for polycrystalline fibers. TlBr-TlI , AgBr , KCl , CsBr , and CsI are mainly studied and various fabrication methods based on crystal growth techniques were proposed. The transmission loss of 0.3 dB m^{-1} was obtained at 10.6 μm wavelength by using a 1 mm diameter CsBr fiber [20]. The advantage of the fibers is that they possess a wide transparency wavelength region from visible to far-IR. This makes it possible to transmit both visible and IR light. On the other hand, the disadvantage is that there is significant loss increase due to plastic deformation caused by repeated bending. Therefore these fibers must be handled carefully.

III INTRINSIC LOSS

IN IR GLASS FIBERS

Glass fibers are the most promising candidates for IR optical fibers. There are many variety of materials that optical fibers can be made from , such as oxides, halides and chalcogenides. In this chapter will discuss intrinsic losses of each fibers.

A. Oxide glass fibers

1. Introduction

In principle, Heavy-metal oxide glasses can be divided into GeO_2 -based and TeO_2 -based glasses. The advantage of heavy-metal glasses such as GeO_2 glass is that since their constituent metals (such as Ge) are heavier than Si in SiO_2 glass. This leads to the ultra-low loss in the IR region. Another advantage of the heavy-metal oxide glass fibers is that almost the same fabrication method as that of the SiO_2 -based glass fibers can be used, so that there is basically no difficulty in fabricating the fibers.

2. Transmission loss

The loss spectra for the GeO_2 -based glass fibers were studied extensively [22,23]. Fig.3.1 shows the loss spectrum for a fiber with a GeO_2 glass cladding. The fiber length is 400 m, and the outer diameter and core diameter are 150 μm and 70 μm , respectively. The numerical aperture NA is 0.11. In the figure, the absorption peaks at 1.4 and 2.2 μm are due to water. The minimum losses of 4 dB km^{-1} at 2 μm and 15 dB km^{-1} at 2.4 μm are obtained.

Fig.3.2 shows the theoretical loss spectrum for GeO_2 -based glass fiber [22]. The loss, less than 0.1 dB km^{-1} , could be achieved around 2.2 - 2.4 μm wavelength [21] and is compare with that of SiO_2 . However another estimation of UV, IR absorptions and Rayleigh scattering revealed that the predicted minimum loss in GeO_2 -based glass fiber is close to 0.25

compare with that of SiO_2 . However another estimation of UV, IR absorptions and Rayleigh scattering revealed that the predicted minimum loss in GeO_2 -based glass fiber is close to 0.25 dB km^{-1} at $2 \mu\text{m}$ [24]. In the latter estimation, the transmission loss of GeO_2 -based glass optical fiber is not superior to that of conventional SiO_2 -based glass fiber.

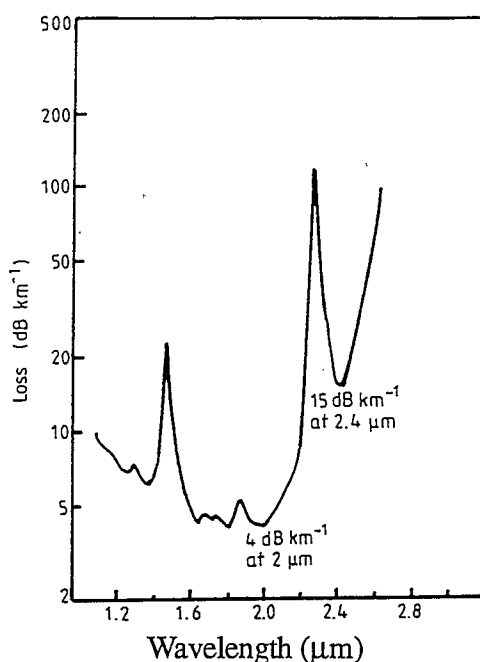


Fig.3.1. The loss spectrum for a fiber with a $\text{GeO}_2\text{-Sb}_2\text{O}_3$ glasses core and GeO_2 glass cladding [after I. Sugimoto].

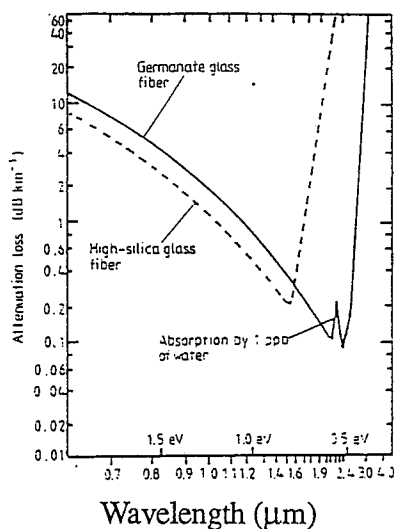


Fig.3.2. The theoretical attenuation loss spectrum of GeO_2 glass optical fiber, together with that already achieved with high-silica fiber [after H. Takahashi].

The transmission loss of TeO_2 -based glass fiber was measured [25]. The loss spectrum for 200 μm diameter TeO_2 -based glass fiber is shown in Fig.3.3. It shows relatively high losses of 1 dB m^{-1} at 2 μm and 20 dB m^{-1} at 4 μm .

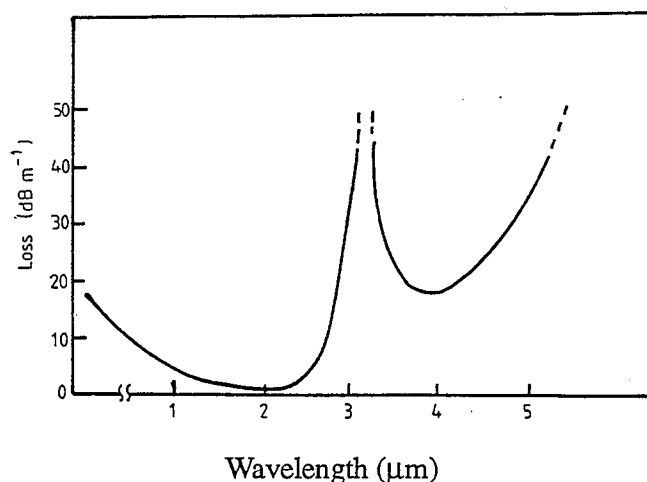


Fig.3.3. The loss spectrum for $(\text{TeO}_2)_{70}\text{ZnO}_{20}\text{BaO}_{10}$ glass optical fiber. The outer diameter is 200 μm [after JY. Boniort].

B. Fluoride glass fiber

1. Introduction

The heavy metal fluoride (HMF) glasses show lesser tendency toward crystallization and higher IR transparency than the BeF_2 - and AlF_3 -based glasses which were discovered before. The HMF glasses can be divided into two distinct categories.

The first category involves fluorozirconate (ZrF_4) or fluorohafnate (HfF_4) glasses. Fluorozirconate glasses are most resistant to devitrification and provide a great deal of flexibility. The second category of HMF glasses excludes ZrF_4 and HfF_4 . Example of this group include the AlF_3 -based glasses, the transition metal fluoride based glasses and rare-earth fluoride based glasses. These glasses, however, are relatively unstable and require rapid

quenching.

2. Transmission loss

Fluoride glasses possess various desirable optical characteristics, such as a broad transparency range from the mid IR to near-UV, low refractive index and dispersion, low Rayleigh scattering, and the potential for ultralow absorption and thermal distortion. In the near-IR to near-UV, fluoride glasses characteristics are similar to those of oxide glasses.

2.1. Transparency of fluoride glasses

Halide glasses offer the potential for very low loss over a broad range of visible and IR wavelengths. Fig.3.4 indicates very low intrinsic loss minima for halide glasses compared to oxides and even chalcogenides. This minimum is determined by the intersection of the Rayleigh scattering loss and the IR absorption edge. The intrinsic minimum loss in HMF glasses is predicted to be 10^{-3} dB km $^{-1}$ at 3.44 μ m compared to 0.16 dB km $^{-1}$ at 1.6 μ m for silica and to 10^{-2} dB km $^{-1}$ at 4.54 μ m for chalcogenide glasses [26].

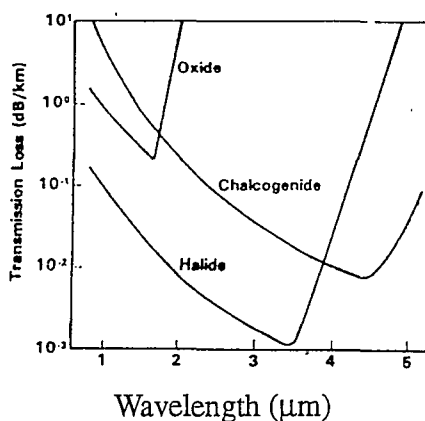


Fig.3.4. Projected minimum of IR glass [after S. Shibata].

The “V-curve” and associated minimum intrinsic loss in the mid-IR of HMF glasses can be estimated by the frequency dependence of the IR edge absorption, and the magnitude of Rayleigh scattering. The V-curves obtained for typical fluorozirconate and BaF $_2$ /ThF $_4$ glasses, assuming a Rayleigh scattering for fused silica, are illustrated in Fig. 3.5 [27]. As indicated, it

should be possible to obtain fluoride glasses whose Rayleigh scattering is lower than that of fused silica. The minimum intrinsic losses predicted in the graphs, 10^{-8} cm^{-1} .

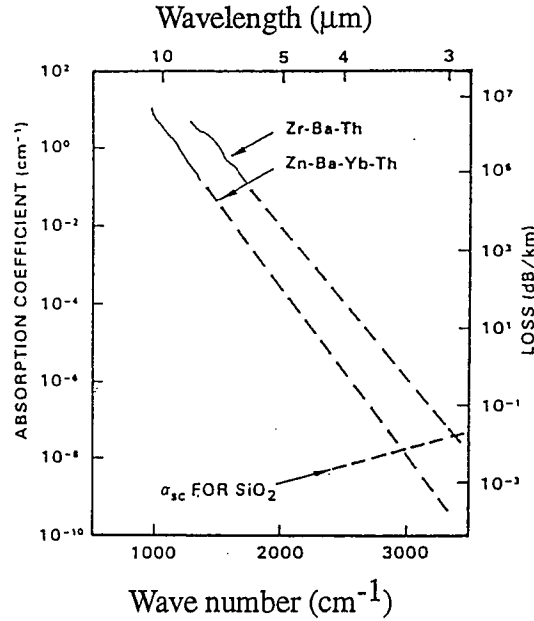


Fig.3.5. IR edges of $58\text{ZrF}_4\text{-}33\text{BaF}_2\text{-}9\text{ThF}_4$ and $26.5\text{ZnF}_2\text{-}17.5\text{BaF}_2\text{-}26\text{YbF}_3\text{-}30\text{ThF}_4$ glasses, and projections to the ultralow-loss region (dash line). The scattering loss for fused silica is also indicated [after M.G. Drexhage].

2.2. IR absorption edge

The IR edge determines the useful range of operating wavelengths for fluoride glass in the IR, and the minimum loss of the V-curve. An understanding of IR edge behavior is important to guide the selection of suitable compositions for IR applications and to obtain reliable projections of the intrinsic absorption in the highly transparent requirement ($\alpha < 10^{-3} \text{ cm}^{-1}$).

In crystalline materials, the IR edge has been shown to come from multiphonon absorption which is depended on frequency and temperature. For example, an analysis has been carried out for typical fluorozirconate to determine the origin and characteristics of their IR edges. Fig.3.6 [30] showed the absorption coefficient α versus frequency for a typical fluorozirconate. The smooth, exponential edge is indicative of the dominant of ionic versus covalent bonding in the glass. In order to establish the edge behavior in more detail, it is

necessary to examine the frequency dependence over a range of temperatures. As shown in Fig.3.7 for a typical HMF glasses [22], α varies fairly smoothly with frequency, decays exponentially with increasing frequency and increases with increasing temperature in a manner characteristic of intrinsic multiphonon absorption [31]. The temperature dependence can be best described using the model for intrinsic multiphonon absorption applied previously to crystalline materials in the near-IR to near-UV, fluoride glasses

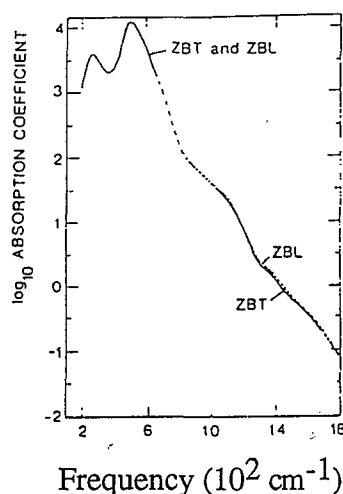


Fig.3.6. IR absorption coefficient versus frequency for ZBL ($60\text{ZrF}_4\text{-}35\text{BaF}_2\text{-}9\text{ThF}_4$) glasses. The dashed line is an extrapolation in between measured portions of the curves [after B. Bendow].

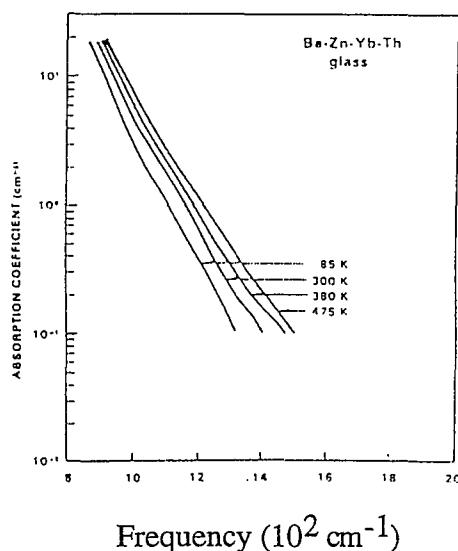


Fig.3.7. IR absorption edge of a $17.5\text{BaF}_2\text{-}26.5\text{ZnF}_2\text{-}26\text{YbF}_3\text{-}30\text{ThF}_4$ glass at several temperatures [M.G. Drexhage].

$$\alpha(\omega, T) = \alpha_o \left[N(\omega_o) + 1 \right]^{\frac{\omega}{\omega_o}} \left[N(\omega) + 1 \right]^{-1} \exp(-A\omega) \quad (2.17)$$

where N is the Bose-Einstein function, α_o is a measure of the vibrational oscillator strength for coupling to light, ω_o is the average vibrational frequency and A is a measure of the vibrational anharmonicity.

Experimental data obtained for α versus T at selected frequencies agree well with the calculated curves, as shown in Fig.3.8 [27], suggesting that simple models based on multiphonon absorption in ionic crystals can be used to interpret and predict the edge behavior of HMF glasses. The projection to lower absorption values using such a model yields the high wavelength side of the V-curves shown earlier in Fig.3.4.

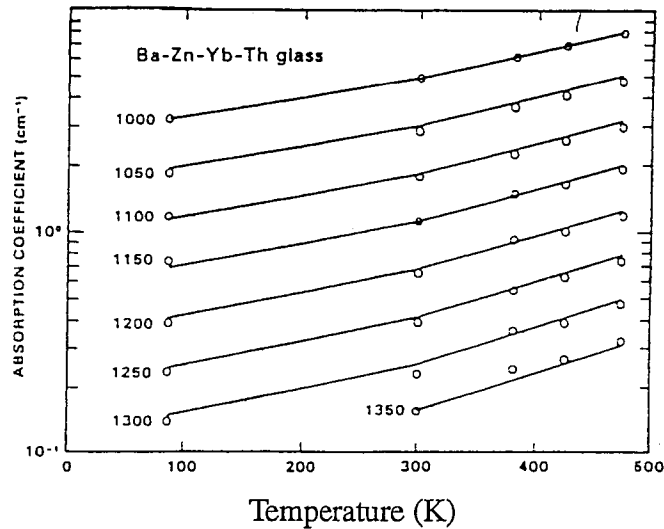


Fig.3.8. Absorption coefficient versus temperatures for a $17.5\text{BaF}_2\text{-}26.5\text{ZnF}_2\text{-}26\text{YbF}_3\text{-}30\text{ThF}_4$ glass. Discrete points are experimental data, and the solid lines are theoretical fit to the data [M.G. Drexhage].

The dependence of the edge properties on compositions is more complicated than for crystals where the reduced mass is the dominant factor. For example, the shift in the IR edge to longer wavelengths for glasses based on hafnium as opposed to zirconium is much smaller

than would be predicted on the basis of the difference in reduced mass. Mixed halide glasses based on CdF_2 appear to have extended long wavelength transparency over both fluorozirconates and rare-earth fluoride glasses, as shown in Fig.3.9 [32].

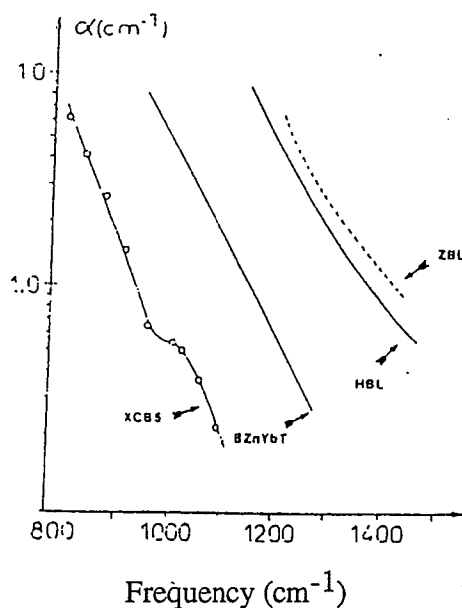


Fig.3.9. Absorption coefficient α versus frequency ν for fluorozirconate (ZBL), fluorohafnate (HBL), $\text{BaF}_2/\text{ThF}_4$ -based (BZnYbT), and CdF_2 -based (XCB5) glasses. The XCB5 glass composition is $65\text{CdF}_2\text{-}2\text{CCl}_2\text{-}33\text{BaCl}_2$ [after M. Matecki].

2.3. UV edge absorption

HMF glasses possess UV edges in the vicinity of $0.25\ \mu\text{m}$ compared to approximately $0.16\ \mu\text{m}$ for fused silica and about $0.15\ \mu\text{m}$ for BeF_2 . The UV edges are extremely sensitive to impurities. Selected HMF glass samples display Urbach tail over several decades of absorption, but most appear to be impurity - dominated. This situation contrasts strongly with the relative insensitivity of the IR edge to processing conditions.

2.4. Scattering loss

The Rayleigh scattering loss (approximately $10^{-4}\ \text{cm}^{-1}$) is not a significant source of

signal attenuation. Rayleigh (elastic scattering varies at λ^{-4}) scattering dominates other intrinsic scattering mechanisms such as Raman or Brillouin scattering. Estimates of Rayleigh scattering may be obtained using the following formula for the loss due to density fluctuation scattering:

$$\alpha_{RS} = \frac{8}{3} \pi^3 n^8 \rho^2 \beta_T k_B T_g \lambda^{-4} = A_{RC} \lambda^{-4} \quad (2.18)$$

where α_T is the isothermal compressibility, ρ is the average photoelastic Pockels constant and k_B is the Boltzmann's constant. Then for typical HMF glasses [26].

$$\alpha_{RS} \approx 0.1 \lambda^{-4} \quad (\text{dB km}^{-1}) \quad (2.19)$$

with $\lambda(\mu\text{m})$. This estimate neglects scattering due to composition fluctuations.

C. Chalcogenide glass fiber

1. Introduction

Over the past two decades chalcogenide glasses have been researched as optical materials for the 8-12 μm wavelength region. For optical applications the chalcogenide glasses possessing the higher resistivities (mainly sulfides, selenides and tellurides) are considered. Generally the sulfides offer some limited visible transmittance and the selenides and tellurides are opaque in the visible region. However, all are transparent in the near and far-IR. For thickness of a few millimeters, sulfides offer transmittance to about 12 μm , selenides to about 15 μm and tellurides to about 20 μm . The IR absorption coefficient ranges from 0.4 to 0.007 cm^{-1} depending upon the wavelength, purity and chemical composition.

1.1. Sulfide glasses

Sulfide glasses are, in principle, divided into two groups: arsenic-sulfur glasses and germanium-sulfur glasses.

The arsenic-sulfur (As-S) glasses are one of the most practical choices of chalcogenide glasses for IR fiber optics. These glasses give a relatively broad range of transmission between 0.6 and 10 μm (when 10 mm thick) and have a relatively high refractive index of 2.41.

Germanium-sulfur (Ge-S) glass, the optical transmission range is almost the same as that for As-S glass, a broad transmission between 0.5 and 11 μm (when 2 mm thick). Ge-S glasses have a relatively lower refractive index of about 2.1.

1.2. Selenide glasses

Various selenide glass systems have been studied mainly in order to achieve lower loss at the wavelengths of 5.4 μm (CO laser) and 10.6 μm (CO_2 laser). Selenide glasses are divided into two groups, one based on As-Se glass and the other on Ge-Se glass.

Selenide glasses have, in principle, a wide transparency region compared to the sulfide glasses. For example, a transmission loss of less than 1 dB m^{-1} has been observed in the wavelength region between 2 and 10 μm [34]. However, selenide glasses tend generally to have a lower softening temperature than sulfide glasses.

1.3. Telluride glasses

The Se-based chalcogenide glasses described above have relatively wide transparent regions. However, their losses at 10.6 μm , which is the wavelength for CO_2 laser light transmission, are still higher than the 1 dB m^{-1} required for practical use. To lower the transmission loss due to the lattice vibration, Te atoms, which are heavier than Se, must be introduced to shift the IR absorption edge toward a longer wavelength. However, Te-based glasses are difficult to form because of their high tendency to crystallization.

2. Transmission losses

2.1. Sulfide glass fibers

These sulfide glass fibers were studied mainly for long haul optical transmission lines, because of the possibility of low loss at 2 - 4 μm wavelength. Furthermore, these fibers are used for transmission lines of CO laser light power (wavelength 5.3 μm).

Measured transmission losses versus photon energy for the $\text{As}_{40}\text{S}_{60}$ bulk glasses (short wavelength region) and optical fibers (long wavelength region) are shown in Fig. 3.10. In the short wavelength region, the loss consists of two exponential parts. The steeper region corresponds to the Urbach tail, which originates from the electronic transition between the valence band and conduction band. The less steep region is due to the weak absorption tail [42]. The transmission loss in the wavelength region longer than 6 μm is mainly due to multiphonon absorption of the glass matrix.

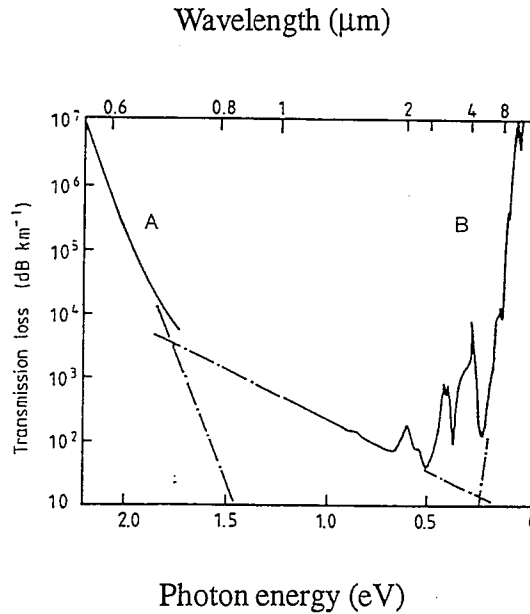


Fig.3.10. Transmission loss versus photon energy for $\text{As}_{40}\text{S}_{60}$ bulk glass (A) and unclad fiber (B) [after T. Kanamori].

The weak absorption loss is the most important for predicting the minimum transmission losses for chalcogenide glass fibers [18]. It is thought that the weak absorption is induced by additional band gap states. The magnitude of the tail depends on the total

concentration of states which cause a weak absorption tail which, in general, are due to impurities or defects. Since the weak absorption tails observed in the chalcogenide glass fibers are related to intrinsic defects in the glasses, it is difficult to reduce the magnitude of the weak absorption tails much below those indicated in Fig.3.10. And it is estimated that weak absorption tails inhibit transmission loss reduction to the level of below 10 dB km^{-1} at the lowest loss wavelengths in chalcogenide glasses fibers. Therefore, it is concluded that these sulfide glass optical fibers are not appropriate for use in long haul optical communication systems [18].

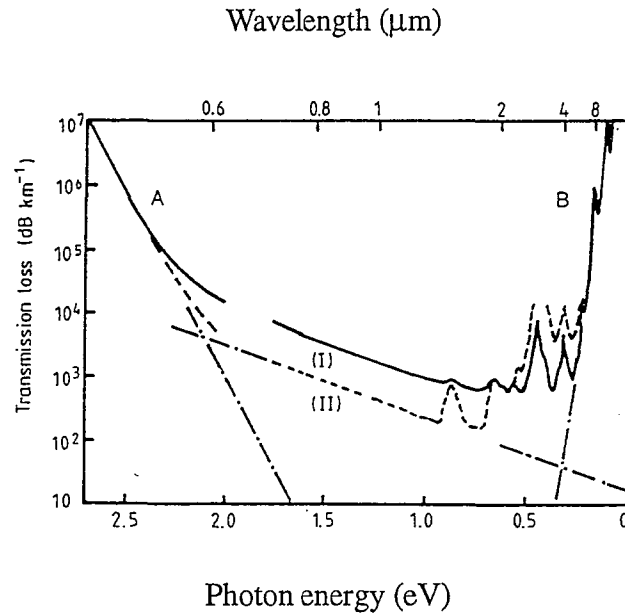


Fig.3.11. Transmission loss versus photon energy for $\text{Ge}_{20}\text{S}_{80}$ bulk glasses (A) and unclad fibers (B). The solid line shows the loss curve for a fiber prepared from a glass with a low hydrogen impurity content (I), while the broken line shows the loss curve of a fiber with a high hydrogen content (II) [after T. Kanamori].

Fig.3.11 shows transmission loss versus photon energy for bulk glass (short wavelength region) and unclad fibers (long wavelength region) with $\text{Ge}_{20}\text{S}_{80}$ [35]. In the figure the solid line shows the loss curve for the fiber with a lower hydrogen impurity content (I), while the broken line shows the loss curve of the fiber with higher hydrogen content (II).

A difference exists in the loss spectra for the two fibers. The loss for the (II) fiber is lower in the short wavelength region, but is higher in the long wavelength region than for the (I) fiber. The higher loss in the long wavelength region for $\text{Ge}_{20}\text{S}_{80}\text{(II)}$ is clearly due to the high level of hydrogen impurity. On the other hand, the short wavelength behavior is attributed to the weak absorption tail, which originates from the gap states. The difference in magnitude of the weak absorption tails shown in the figure indicates that hydrogen impurities may decrease the number of gap states.

2.2. Selenide glass fibers

The most interesting application of selenide glass fiber is in CO_2 laser light transmission, of wavelength $10.6\text{ }\mu\text{m}$. Selenide glass fibers can be classified into As-Se, Ge-Se and As-Ge-Se based glass fibers.

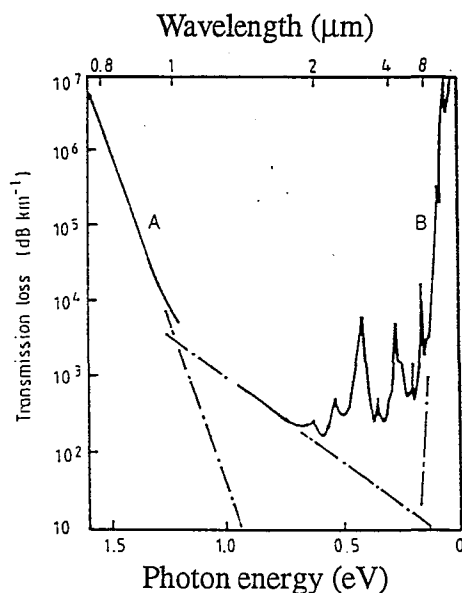


Fig.3.12. Transmission loss versus photon energy for $\text{As}_{38}\text{Ge}_5\text{Se}_{57}$ bulk glass (A) and unclad fiber (B) [after T. Kanamori].

As-Ge-Se glass, Fig.3.12 [35] shows the transmission loss spectrum obtained for $\text{As}_{38}\text{Ge}_5\text{Se}_{57}$ bulk glass ($< 0.7\text{ }\mu\text{m}$) and optical fiber ($> 1\text{ }\mu\text{m}$). The loss spectrum consists of Urbach tail ($< 0.7\text{ }\mu\text{m}$), weak absorption tail ($0.7 - 2\text{ }\mu\text{m}$), impurity absorption peaks and

multiphonon absorption ($> 2 \mu\text{m}$). Also, [42] it was shown that the loss depends strongly on temperature and increases with it. It is known that the temperature change causes the shift of the multiphonon absorption band and the loss at the tail of the absorption decreases with decreasing temperature. It was found from the experiment that the temperature change of transmission loss for a selenide fiber is larger than that for other materials.

The loss spectrum of a $\text{Ge}_{20}\text{Se}_{80}$ glass fiber is shown in Fig.3.13. Results show that the transmission loss is less than 1 dB m^{-1} for the wide IR region. The minimum loss is 0.2 dB m^{-1} at $5.5 \mu\text{m}$. Fig.3.13 also shows that the loss is relatively high in the wavelength region above $9 \mu\text{m}$. The loss at $10.6 \mu\text{m}$ (CO_2 laser wavelength) is as high as 8 dB m^{-1} . These losses are mainly due to intrinsic Ge-Se lattice vibrations.

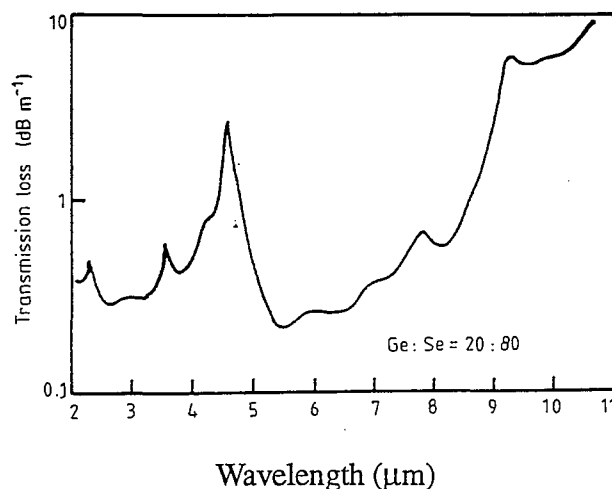


Fig.3.13. The transmission loss spectrum for $\text{Ge}_{20}\text{Se}_{80}$ chalcogenide glass fiber [after H. Mori].

2.3. Telluride glass fibers

Telluride glass fibers are thought to be advantageous in lowering the loss at a $10.6 \mu\text{m}$ wavelength because the heavy Te atoms have the effect of shifting the absorption band due to lattice vibration toward longer wavelengths. Moreover, the absorption peak at 13

μm decreases. However, as the Te content increases, it may become more difficult to draw into glass fibers without yielding microcrystals.

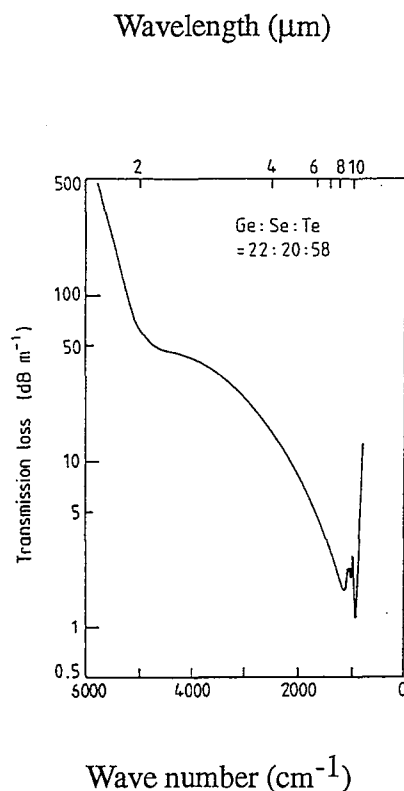


Fig.3.14. The transmission loss spectrum for $\text{Ge}_{22}\text{Se}_{20}\text{Te}_{58}$ glass optical fibers [after T. Katsuyama].

The transmission loss of the $\text{Ge}_{22}\text{Se}_{20}\text{Te}_{58}$ glass fiber is shown in Fig.3.14. The loss at wavelengths below $2 \mu\text{m}$ is due to the Urbach tail, while that at wavelengths above $10 \mu\text{m}$ is due to lattice vibrations. The loss in the wavelengths between 2 and $10 \mu\text{m}$ is attributed to Mie scattering caused by the few microcrystals which remain in the glass. Mie scattering is defined as scattering caused by scattering centers whose dimensions are of the same order of magnitude as the light wavelength. The wavelength dependence of this loss is shown in Fig.3.15. The figure confirms that loss changes linearly with the wavelength to the power -3 . It is also found that the loss increases as the Te content increases.

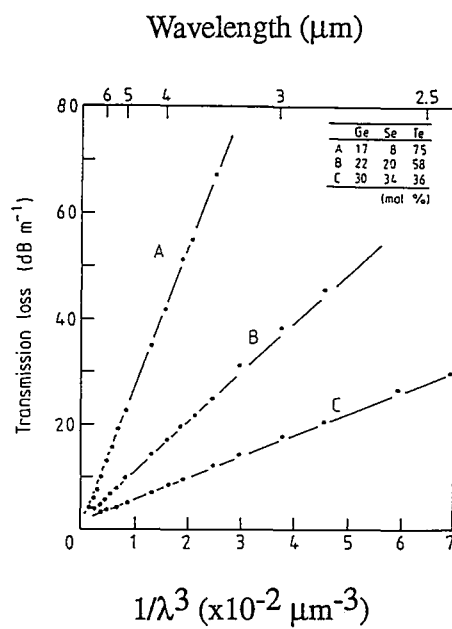


Fig.3.15. Transmission loss versus $1/\lambda^3$ (λ is wavelength) for three Ge-Se-Te glass optical fibers [after T. Katsuyama].

IV INTRINSIC LOSS

IN IR CRYSTALLINE FIBERS

A. Introduction

Crystalline fibers can be divided into two categories; polycrystalline (PC) fibers and single crystal (SC) fibers. TlBr-TlI (KRS-5), silver halides and cesium halides are used as materials for crystalline fibers. In this chapter will be discussed each of those crystalline fibers.

B. Polycrystalline fibers

Polycrystalline fibers show low loss in the wavelength region above 10 μm . Therefore, the main target for these fibers is used in the power transmission of CO_2 laser light (wavelength 10.6 μm), which is an important application in the fields of laser surgery and laser welding. The main materials studied so far are TlBr - TlI. Other materials for polycrystalline fibers are AgCl, AgBr, and AgCl-AgBr mixed crystal. The properties of these materials are similar to these of TlBr-TlI mixed crystal. The advantage of these materials is that they show a high tensile strength. KCl, NaCl, CsI and KBr have also been studied for polycrystalline fibers.

1. Transmission loss

Theoretical analysis shows that the minimum intrinsic loss for crystalline fibers is extremely low. It was [44] predicted that halide compounds such as TlBr and TlBr-TlI have a transmission loss of $10^{-2} - 10^{-5} \text{ dB km}^{-1}$ in the spectral region of above 4 μm . However, the minimum loss so far obtained is about 0.1 dBm^{-1} [44], which is 10^4 times larger than the predicted value. This is mainly due to scattering loss caused by the various scattering centers in the crystals.

The relation between the transmission loss and the wavelength for the TlBr - TlI

polycrystalline fibers in shown in Fig.4.1 [23]. In the figure, the solid line shows the theoretically estimation of the transmission loss, while the dots show the experimental results. As shown, even though the estimation shows the minimum loss of less than 10^{-2} dB km⁻¹ at a 7 μ m wavelength, the minimum loss of the measured fiber is about 100 dB km⁻¹, which takes place in the wavelength region of 20 μ m [39]. The large discrepancy between the estimation and the measured value can be explained in terms of the scattering due to both the irregularity at the interface of the core and the crystal defects introduced during the fiber fabrication process.

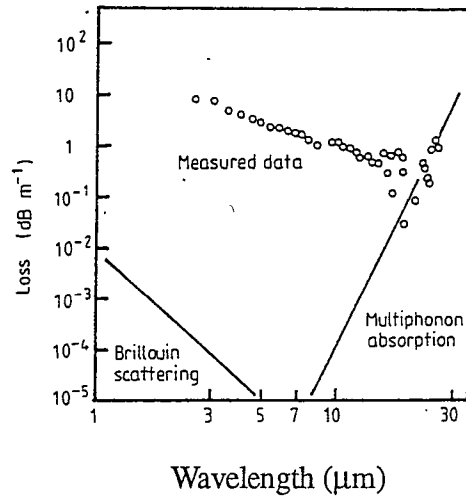


Fig.4.1. The transmission loss spectrum for polycrystalline TlBr-TlI fiber. The solid lines show the theoretical estimate of the transmission loss[after I. Sugimoto].

Fig.4.1 also shows that the transmission loss is inversely proportional to the wavelength to the power 2 [40]. This means that the loss originates from Mie scattering.

C. Single crystalline fibers

Single crystals are an ideal material from the viewpoint of intrinsic transmission loss, because Rayleigh scattering of single crystal is generally one tenth as small as that of amorphous materials. The weak absorption tail is also important in determining the transmission loss of single crystalline fibers, such as alkali halide crystals. Other than the

optical loss viewpoint, single crystalline fibers possess a wide transparent wavelength region from visible to far-IR. Although the intrinsic absorption loss of alkali halide materials is estimated to be very small, they can not be obtained in the amorphous state. So these materials must be used in a crystalline state. However, the fabrication techniques of single crystal fibers have not been well developed.

The materials used for single crystalline fibers are basically the same as those used for the polycrystalline fibers. Today the most important SC fibers is sapphire (Al_2O_3) [37]. Sapphire fibers are not transparent at $10.6\ \mu\text{m}$. Halide compounds such as KCl, CsBr, CsI, AgBr and TlBr-TlI (KRS-5) have been studied. Materials other than halide compounds, such as Al_2O_3 , Nd:YAG and LiNO_3 , have been studied.

1. Transmission loss for halide fibers

Because only a few papers describing the transmission losses of single crystalline fibers other than halide fibers have written, the following section will discuss only halide single crystalline fibers.

Mori and Uzawi reported an interesting result on the absorption coefficients of LiF, BaF_2 , CsI, KCl, TlBr-TlI and SiO_2 glass (all crystalline forms, except SiO_2). Their results are shown in Fig.4.2, where the solid lines represent the data reported before their measurement. TlCl-TlBr have some absorption tail which is observed below $1.5 \times 10^{-1}\ \text{cm}^{-1}$ in the absorption coefficient. Other materials have similar characteristics in the visible wavelength region. These measured absorption tails can be expressed by

$$\alpha = \alpha_0 \exp\left(\frac{h\omega}{2\pi E}\right) \quad (2.20)$$

where α is the absorption coefficient, $h\omega/2\pi$ is the photon energy, α_0 and E are constants.

E for the absorption tails have almost the same value in the range 0.3 - 0.5 for both crystalline and amorphous materials, except for BaF_2 . These absorption tails are called weak absorption tails [42], and are caused by defects, disorder, and impurities. It should be noted that the weak absorption tail can be found even in high purity materials, such as NaCl crystal

and silica glass.

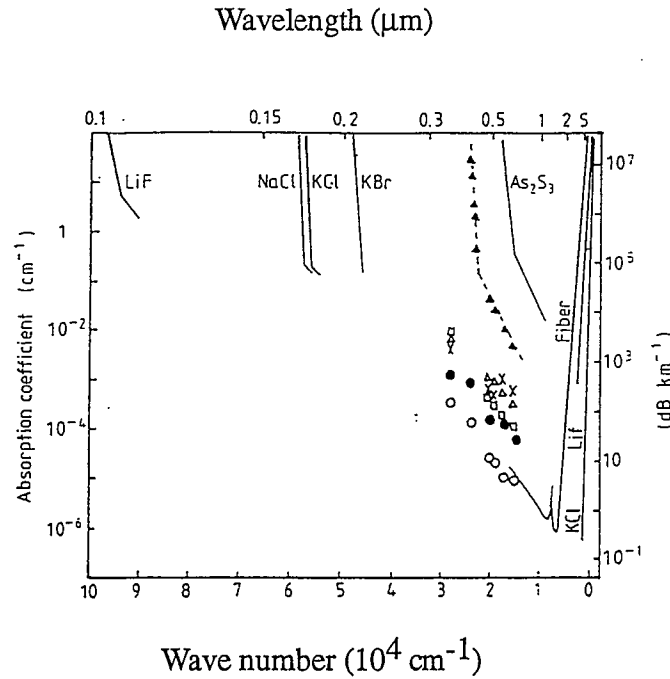


Fig.4.2. Measured absorption coefficients versus wavenumber for LiF, KCl, CsI, KRS-6 (TlCl-Br) and SiO₂ (▲, KRS-6; ×, BaF₂; △, KCl; □, CsI; ○, LiF; ●, SiO₂) [after H. Mori].

It can also be seen from Fig.4.2 that the total loss in the wavelength region 0.4 - 2 μm depends mainly on the weak absorption tail, because this slope is flatter than that of multiphonon absorption. Therefore, [41] the weak absorption tail plays an important rule in determining the transparency limitation for low loss materials, particularly materials for IR optical fibers.

V SUMMARY

Intrinsic loss mechanisms for IR materials used for optical fibers must be determined to obtain the minimum intrinsic loss which is involved in choosing suitable IR materials for fabricating IR optical fibers. In each fiber, the intrinsic loss mechanisms is different depending on their intrinsic material properties. IR optical fibers can be categorized into glass fibers and crystalline fibers.

For heavy metal oxide glasses, GeO_2 is thought to be good candidate for ultra low loss optical fibers. The advantage of heavy metal oxide glass, such as GeO_2 , is that since their constituent metal (such as Ge) are heavier than Si in SiO_2 glass, IR absorption due to lattice vibration (Ge-O) can be shifted toward a longer wavelength. This leads to the ultra-low loss in the IR region. The minimum loss so far reported for GeO_2 is less than 0.1 dB m^{-1} around $2.2 - 2.4 \text{ }\mu\text{m}$. However the estimation of UV and IR absorptions and Rayleigh scattering shows that the predicted minimum loss in GeO_2 -based glass fiber is close to 0.25 dB km^{-1} at $2 \text{ }\mu\text{m}$. In this estimation, its transmission loss is not superior to that of SiO_2 glass fibers.

Fluoride glass fibers offer the best properties of ultra low loss optical fibers whose transmission loss is lower than that of the high silica glass fiber. It has broad transparency range from mid-IR to near-IR, and low Rayleigh scattering. The materials that have been studied so far are fluorozirconate and fluorohafnate glasses. IR edge properties are investigated and come from multiphonon absorption which depends on frequency and temperature. The UV edge and Urbach tail appear to depend on impurities. Rayleigh scattering loss is not the important factor in fluoride glass fibers.

Chalcogenide glass fibers studied so far can be divided into two groups: sulfide glass fibers and selenide and telluride glass fibers. All are transparent in the near and far IR. The transmission loss of sulfide glass fiber has been reduce to less than 0.1 dB m^{-1} at $2 - 5 \text{ }\mu\text{m}$. However, further loss reduction is thought to be difficult because of the existence of the intrinsic weak absorption tail. Selenide and telluride glass fibers have transmission loses of

about 1 dB m^{-1} .

Polycrystalline fibers are classified into thallium halides and silver halides, which are characterized by their ductile properties. The main transmission loss come from Mie scattering which has a wavelength dependence of λ^{-2} . Therefore the transmission loss is low in the wavelength region of more than $10 \text{ }\mu\text{m}$, which is useful for transmitting CO_2 laser light. A loss as low as 0.1 dB m^{-1} at a $10.6 \text{ }\mu\text{m}$ have been achieved.

Material used for single crystalline fibers are almost the same as those for polycrystalline fibers. Transmission loss of 0.3 dB m^{-1} was obtained at a $10.6 \text{ }\mu\text{m}$ by using a CsBr fiber. These fibers posses a wide transparency region from visible to far-IR but there is significant loss increase due to the plastic deformation caused by repeated bending.

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