Refractive Index of Silica Glass in the UV Region

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(Abstract)

The refractive index of several silica glasses (type III, IV and Sol-Gel) has been measured in the UV region. A linear relationship is observed between the refractive index and the density of these glasses. Differences in the number of oxygen deficient centers (SiO_x) and OH species are thought to give rise to this linear relationship. The temperature dependence of the refractive index is concluded to be caused by a temperature shift of the exciton reflection peak at around 10.4 eV, which shifts toward the low energy side at a rate of 0.23 meV/K.

1.Introduction

Silica glass has many important applications in the UV region because of its high transparency and durability against UV light shorter than 300 nm. However, the refractive index of the glass differs from sample to sample depending on the fabrication method(1). The index difference can be as large as $\Delta n=\pm1\times10^{-4}$ in the UV region, ten times as large as that required for precise optics such as UV cameras, telescopes, microscopes and stepper lenses. Several reasons that could cause this distribution are differences in density and impurity content(2,3). The present paper discusses the distribution of refractive index in relation to the density of glasses containing OH species at various concentrations and prepared by different methods and conditions. The refractive index of glasses that were densified by using a high pressure apparatus are also discussed in relation to their density.

Furthermore, the refractive index and dispersive power depend on temperature more strongly in the UV region than in the visible region(4). This will also cause problems in the focusing and achromatizing properties of the UV lenses. The origin of the temperature dependence of the refractive index is discussed in terms of the temperature dependence of the reflection spectrum of the glass in the vacuum ultra-violet (VUV) region. The temperature coefficient of the dispersive power is calculated from the observed value of dn/dT by using a dispersion formula instead of the Abbe number which is useful only in the visible region.

2. Density Dependence of Refractive Index

The refractive index of silica glasses (type III, IV and Sol-Gel) has been measured at several spectral frequencies emitted from a Hg-lamp by using the minimum deviation method with a precision of $\Delta n=\pm 1\times 10^{-5}$ at 25.0 ^{o}C. The density has been measured by the Archimedes method in distilled water with a precision of $\Delta\rho=\pm 3\times 10^{-4}$ (g/cm^3). Fig.1 shows the density dependence of the refractive index at 248 nm for thirteen glass samples including type III (open circle), type IV (closed marks) and Sol-Gel (triangle) glasses. The type IV glasses were prepared under three different conditions, each of which is shown in the figure by a different type of closed mark for distinction. The sample (type IV) with an asterisk sign contains chlorine impurities around 1,000 ppm. In the other twelve samples, the chlorine content is less than 100 ppm, while the OH content ranges from 40 to 1200 ppm. The OH content is shown in the figure in ppm for each sample. The glasses were well annealed prior to the measurements to achieve optical homogeneity better than $\Delta n=1\mathrm{x}10^{-6}$ cm^{-1}.

The figure shows that the refractive index of silica glass has a linear relationship with density when the chlorine content is less than 100 ppm. The linear coefficient (slope) at 248 nm is about 0.11 (cm^3/g).

In order to gain further insights into the origin of the linear relationship between the refractive index and density, samples were densified by using a hot isostatic pressing (HIP) apparatus. Cubic glass blocks of 5 cm each length were densified under an operating pressure and temperature of 1,500-2,000 $\mathrm{kgf/cm}^2$ and 1,100-1,200 ^{0}C, respectively. Prism samples with an apex angle of 60^0 and square faces of 3 cm each length were prepared from the blocks after removing the surfaces contaminated with argon gas that had diffused into the glass during the HIPping process. The prisms were free from substantial argon contamination and were optically homogeneous to better than $\Delta n=1\mathrm{x}10^{-6}$ cm^{-1}.

Fig.2 shows the refractive index at 248 nm in the densified states for type III (open circle) and IV (closed circle) glasses. The ρ-n relation for the un-densified glasses is also shown with a thin dotted line for comparison. For both of the densified glasses, linear relations are observed between density and refractive index with a larger linear coefficient (0.26 cm^3/g) than that of un-densified glasses. Furthermore, the ρ-n lines for the two types of densified glasses are parallel within experimental error.

For the densified glasses, the linear ρ-n coefficient and its wavelength dependence are well explained by the extended point dipole theory as an increase in the number of SiO_4 units per unit volume(5,6). On the other hand, glasses with different fictive temperatures are known to show a similar ρ-n relation with a linear coefficient close to that of the densified samples (2), indicating that the effect of fictive temperature is closely related to the densification phenomena. Therefore, the ρ-n relation observed in the non-densified glasses should have origins other than changes in packing density or differences in the fictive temperature. Possible origins are the presence of oxygen deficient centers like SiO_x $(0 \leq x < 2)$ and the presence of OH species in the glass. In fact, the density and refractive index are known to increase when SiO_x centers are created in the glass under the irradiation of strong UV light(7).

Of these two possibilities, the effect of SiO_x species seems to be of primary importance, since the density and refractive index depend on the fabrication methods or conditions for glass preparation as was shown in Fig.1. The SiO_x content is thought to depend on the atmosphere in which the glasses were synthesized or sintered. Type IV glass is sintered in a strong reducing atmosphere and would include SiO_x at a higher concentration than type III glass, resulting in a higher density and refractive index than those of type III. The concentration of OH species, on the other hand, seems to be of secondary importance in affecting the density and refractive index, since the density of some glasses with high OH content can be higher than that of glasses with low OH content as is seen in the results for type Ⅳ glasses that are synthesized under different conditions. At a fixed processing condition, however, the density and refractive index decrease as the OH content increases. Depending on the content of OH species in the glass, some of the oxygen deficient centers could be converted into oxy-hydride centers which would have a molar volume and refractivity close to those of SiO_4 units.

In addition to scientific interest, the ρ-n relation in Fig.1 is of practical importance because it gives us a convenient method to estimate the refractive index of silica glass from its density. Although the precision of the estimation at present is limited to $\Delta n=\pm 4x10^{-5}$ at 248 nm, the method will become practically useful if the density can be measured with a precision of $\Delta\rho=\pm 1x10^{-4}$ (g/cm^3) which is one third of the present error range.

3. Temperature Dependence of Refractive Index and Dispersive Power

The temperature dependence of the refractive index (dn/dT) has been measured for three types of glasses (type Ⅲ, Ⅳ and Sol-Gel) at temperatures ranging from 100 to 350 K. No significant differences were observed in dn/dT between the glasses, although the absolute value of n depends on the preparation method as explained above. Fig.3 shows the temperature dependence of refractive index at several wavelengths (Hg-546,365,248 nm) for type Ⅲ glass. In Fig. 3, the refractive index is plotted as the difference n(T)-n(275.5 K) for easy comparison, rather than as an absolute index value. In Fig.4, values of dn/dT at Hg-546,365 and 248 nm are plotted versus temperature in the region from 100 to 350 K. The values of dn/dT near room temperature are in good agreement with previously reported values(4), although the data in Ref. (4) are given in relative refractive indices in the region 26-828 ^{0}C.

In order to explain the origin of the temperature dependence of the refractive index, the reflection spectrum of silica glass was measured in the VUV region. In Fig.5, the reflection spectra of type Ⅲ silica glass at 299 K and 82 are shown. The spectra were measured by using synchrotron orbital radiation as a light source. It can be seen that the first exciton peak around 10.4 eV shifts toward the high energy side by about 50 meV without any change in reflection intensity when the samples are cooled from 299 K to 82 K. The average temperature shift is about 0.23 meV/K. The second broad band around 11.6 eV seems to change neither its position nor its intensity. Therefore, the temperature shift of the exciton peak is likely to be the origin of the temperature dependence of refractive index. This hypothesis could be checked by calculating refractive indices from the reflection spectra by using the Kramers-Kronig analysis, provided that the observed reflection intensities were true ones without any surface scattering or contamination. However, for our samples this is not the case. The reflectivity of the first peak showed fluctuations of a few percent centered around 20 % depending on the surface finish of the sample, although the peak position was not changed. Therefore, it is not easy to obtain the true reflectivity and to calculate the refractive index through the Kramers-Kronig analysis.

Instead of the K-K analysis, we used the three term Sellmeier equation (1,8), which consists of an absorption band around 0.13 eV in the IR-region and two bands around 10.7 and 18.1 eV in the VUV region. The peak position and intensity in the equation were determined by the least squares method in order to fit the absolute refractive indices at 20.5 ^{0}C in the wavelength region from 0.237 to 1.71 μm. After determining the six parameters at 20.5 ^{0}C, only the one parameter that defines the position of the first VUV peak around 10.7 eV can be shifted toward the low energy side at the experimentally observed rate of 0.23 meV/K without changing the absorption intensity. Fig.6 is a comparison between the experimental dn/dT values at 196 K and the predicted values from the Sellmeier analysis at the same temperature. The agreement is excellent in spite of the rough approximation used here. Therefore, it is concluded that the origin of the temperature dependence of the refractive index is the temperature shift of the first reflection band around 10.4 eV, which shifts toward the low energy side by 0.23 meV/K when the temperature increases. Furthermore, the temperature dependence of the refractive index is well expressed by the three term Sellmeier equation with one term containing a temperature shift of the resonance energy at the rate of 0.23 meV/K.

As for the temperature dependence of the dispersive power, it is better to define a new equation for the dispersive power in the UV region, because the Abbe number is useful only in the visible region. In principle, the dispersive power can be defined as $(dn/d\lambda)/(n-1)$ by taking the derivative of the Sellmeier equation if the six parameters of the equation are known from the refractive indices at six or more wavelengths. However, this procedure is somewhat laborious.

Instead of $(dn/d\lambda)/(n-1)$, we would like to propose a new equation for the dispersive power as

$$1/\nu_{1,2}=\ln((n_1-1)/(n_2-1)),$$

where n_1 and n_2 are the refractive indices at wavelengths λ_1 and λ_2, respectively. This equation can be derived quite easily from the definition of Abbe number by generalizing the wavelengths as follows;

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

$$1/\nu_0=(n_1-n_2)/(n_0-1)=\Delta n/(n_0-1)=\Delta\ln(n_0-1),$$

where

$$\lambda_1<\lambda_0<\lambda_2,\ \text{and}\ |\lambda_1-\lambda_2|\ll 1.$$

The new equation needs only two refractive indices at wavelengths λ_1 and λ_2, and in fact is found to reproduce the Abbe number to a good approximation when n_F and n_C are used in the equation as n_1 and n_2, respectively.

In the UV region, we can use two spectral lines emitted from a Hg-lamp near 248 nm (KrF laser), one at 238 nm (λ_1) and the other at 275 nm (λ_2). Fig.7 shows the temperature dependence of dispersive power ($\nu_{1,2}$) defined by the new equation. When the temperature increases, the dispersive power decreases while refractive index at 248 nm increases. These temperature dependences should be properly taken into account when designing a thermally stabilized achromatic lens system.

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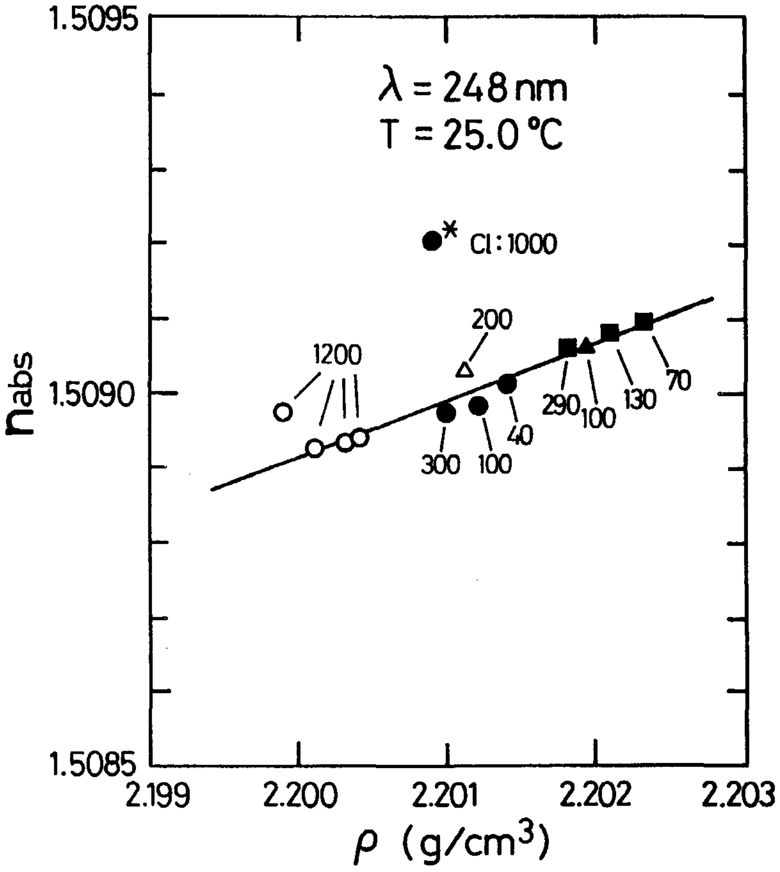

Fig.1 Density and refractive index of type Ⅲ (○), Ⅳ (●, ■, ▲) and Sol-Gel (△) glasses. OH concentrations for each sample are also shown.

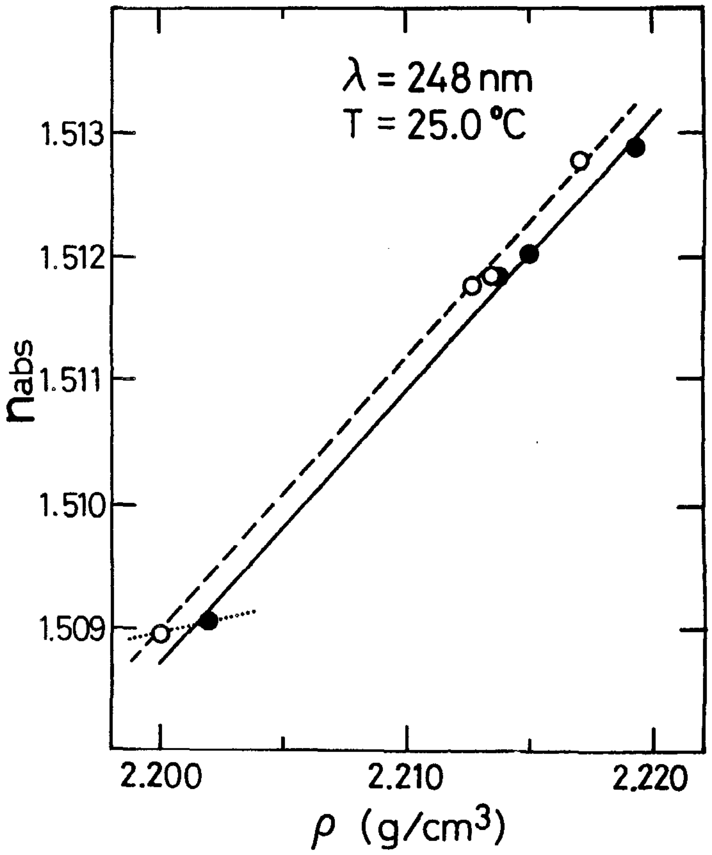

Fig.2 Density and refractive index of densified glasses.

○ ; type III , ● ; type IV.

The ρ-n relationship for un-densified glasses is shown with a dotted line for comparison.

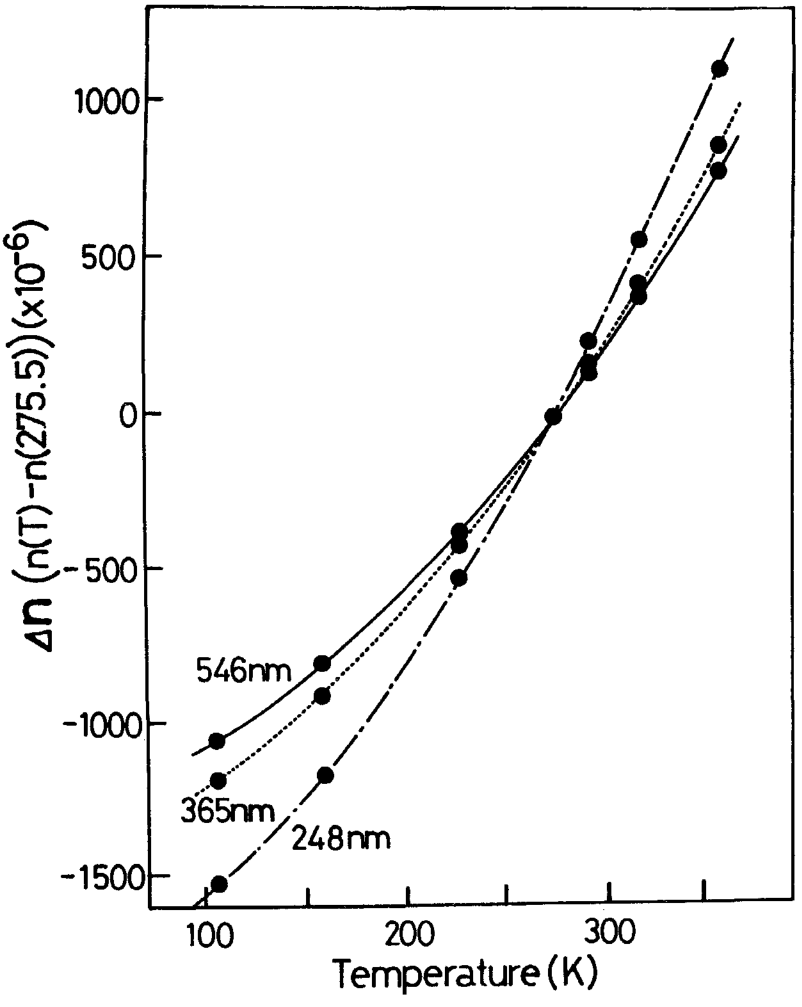

Fig.3 Temperature dependence of the refractive index of type Ⅲ silica glass at Hg-546, 365 and 248 nm.

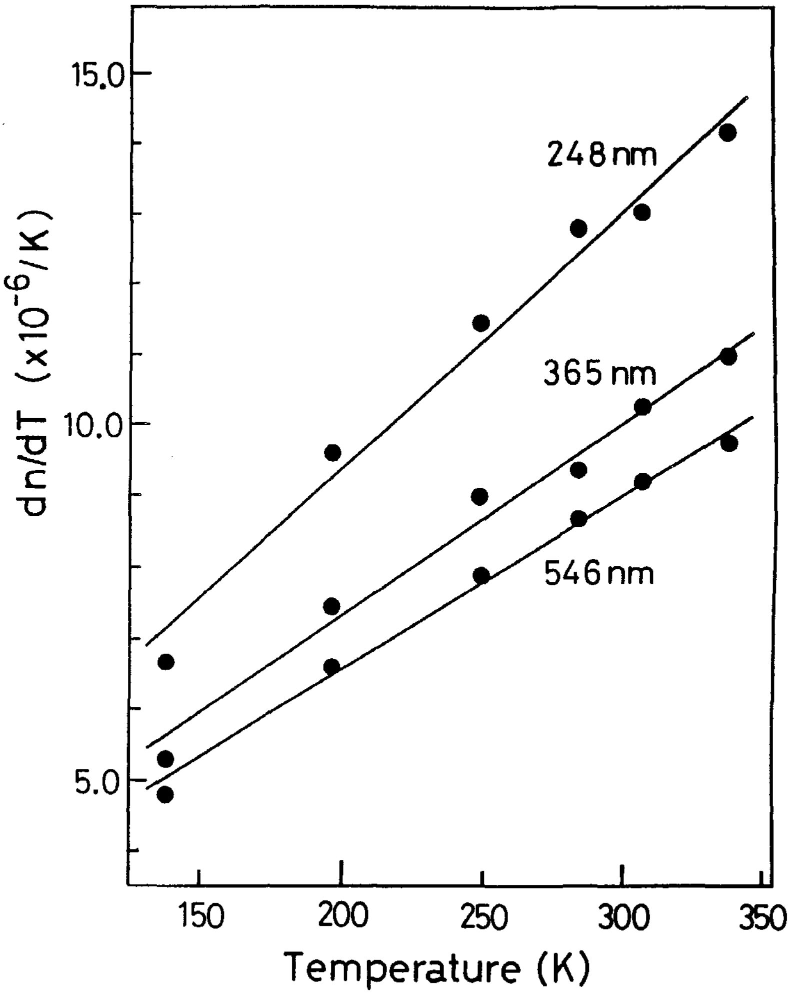

Fig.4 Temperature coefficient of the refractive index (dn/dT) of type Ⅲ glass at Hg-546, 365 and 248 nm.

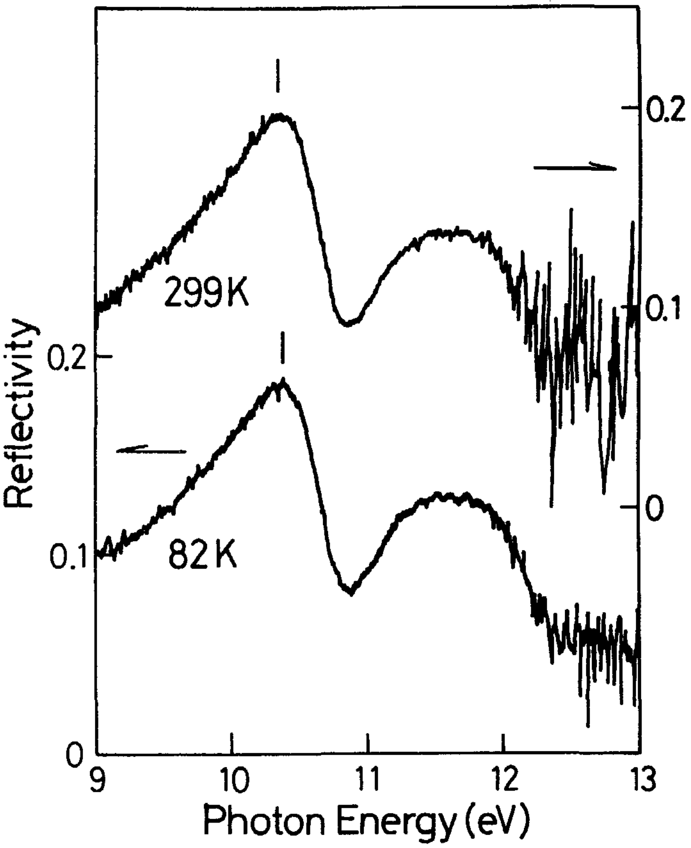

Fig.5 Reflection spectra of type Ⅲ silica glass at 299 K and 82 K.

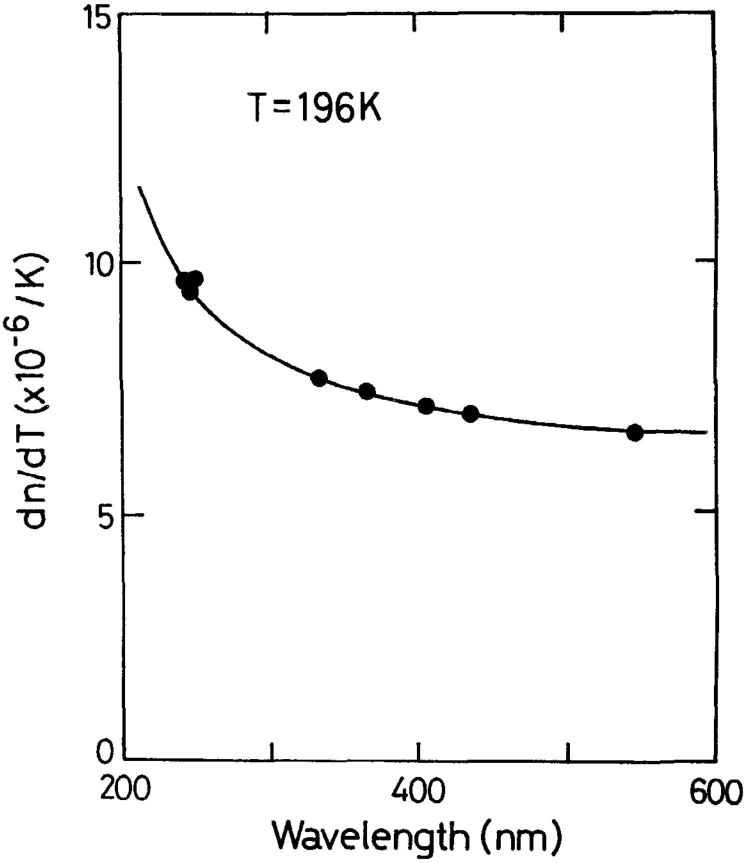

Fig.6 Comparison between temperature coefficients measured and calculated at 196 K for type Ⅲ silica glass.

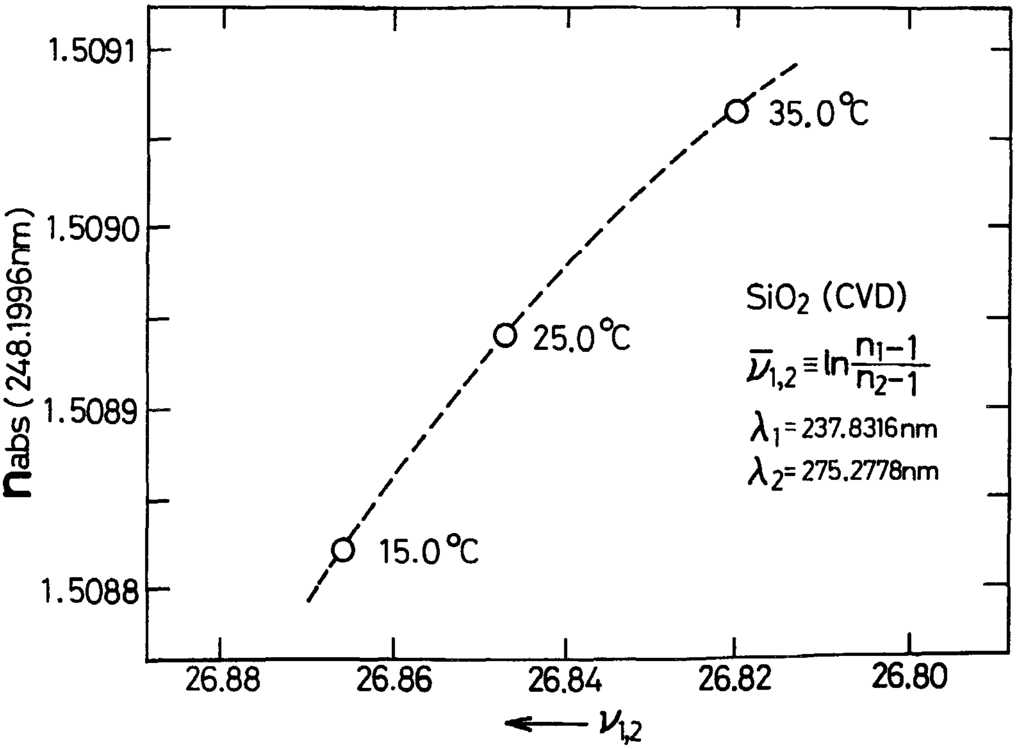

Fig.7 Temperature dependence of refractive index (n_{248})and dispersive power ($\nu_{1,2}$) of type Ⅲ glass.