Original Paper

Does Shelyubskii's evaluation method characterize the homogeneity of glass?[1)]

Hans-Jürgen Hoffmann

Institut für Nichtmetallische Werkstoffe: Glaswerkstoffe, Technische Universität, Berlin (Germany)

A formula given by Shelyubskii has been used in several publications to characterize the homogeneity of glasses from internal spectral transmittance curves of Christiansen filters. It is shown that this evaluation method cannot provide any useful data on the homogeneity of glass.

Kann die Glashomogenität nach der Shelyubskii-Formel bestimmt werden?

In mehreren Publikationen wurde die Homogenität von Glas aus dem internen spektralen Transmissionsvermögen von Christiansen-Filtern mit Hilfe einer Formel von Shelyubskii bestimmt. Es wird gezeigt, daß mit dieser Auswertemethode keine brauchbaren Ergebnisse über die Homogenität von Glas erhalten werden können.

1. Introduction

According to a recent paper [1], Raman's theory [2] fails to characterize the internal spectral transmittance curves of Christiansen filters correctly. On the other hand, Raman's formula has been extended by Shelyubskii to characterize the inhomogeneity of glasses from such transmittance curves. According to [3], the internal transmittance T of Christiansen filters made of powder of inhomogeneous glass is given by

$$T = \exp(-k^2 \pi^2 \lambda^{-2} \bar{d} z (\Delta n^2 + \sigma^2)) \quad (1)$$

with the constant k^2 depending on the shape of the grains and on the packing density, the wavelength λ, the average diameter of the grains $\bar{d}$, the thickness of the filter z, the difference Δn of the refractive indices between the glass grains and the immersion liquid, and σ^2 is the "square of the standard deviation of the refractive index from the mean value $\bar{n}(\lambda)$", i.e.,

$$\sigma^2 = \frac{1}{V_0} \int_{V_0} (n(\lambda, V) - \bar{n}(\lambda))^2 \, \mathrm{d}V, \quad (2)$$

where $\mathrm{d}V$ is the volume element and V_0 is the total volume under consideration. σ^2 is considered to be approximately independent of the wavelength since the inhomogeneities are presumed to shift essentially the dispersion curve $n(\lambda)$ of the glass parallel to the n axis. For $\sigma^2 = 0$ equation (1) corresponds to Raman's formula [2]. Since it was shown in [1] that various experimental characteristics of the spectral transmittance curves of Christiansen filters using powder of the optical glass K5 [4] are not correctly described, one would also expect that equation (1) is not adequate to characterize the homogeneity of the refractive index. Nevertheless, equation (1) has been applied in several publications [5 to 11] to quantify the homogeneity of glasses from the spectral transmittance of Christiansen filters without and with questioning the reliability of the evaluation method.

In order to clarify the situation, the relevance of equation (1) for the determination of the homogeneity of glasses from the spectral transmittance curves of Christiansen filters is investigated in the present paper. The author does not consider in detail the practical problems of determining and evaluating the transmittance curves of Christiansen filters as a function of the wavelength nor the basics for a theory.

2. Shelyubskii's evaluation of the spectral transmittance curves of Christiansen filters

From a mathematical point of view one can characterize the homogeneity from equation (1) in a straightforward manner irrespective of its validity: the transmittance reaches its maximum

$$T_{\max} = \exp(-k^2 \pi^2 \lambda^{-2} \bar{d} z \sigma^2) \quad (3)$$

for $\Delta n^2 = 0$. The value of half maximum

$$T_{\max}/2 = \exp(-k^2 \pi^2 \lambda^{-2} \bar{d} z (\Delta n_{1/2}^2 + \sigma^2)) \quad (4)$$

Received 2 October 1998.

[1)] Presented in German at: 72nd Annual Meeting of the German Society of Glass Technology (DGG) in Münster (Germany) on 27 May 1998.

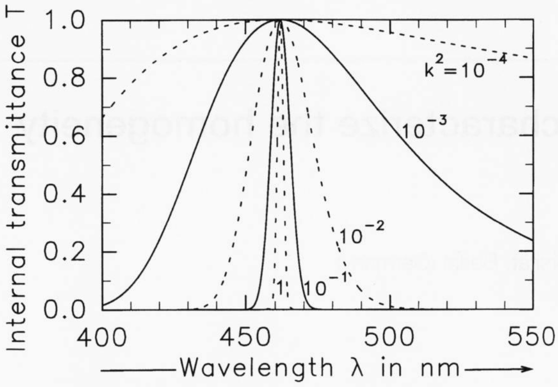

Figure 1. Theoretical internal transmittance of Christiansen filters made of homogeneous glass as a function of wavelength, λ, according to Raman's formula (equation (1) with $\sigma^2 = 0$) for different values of k^2. Parameters: z = 5 mm, $\bar{d}$ = 0.19 mm; the data of the refractive indices are taken from [1].

defines two solutions for the difference between the refractive indices of the liquid and the glass grains. Neglecting small corrections for λ^2 in the denominator of the argument of the exponential, one obtains from equations (3) and (4)

$$\sigma^2 = (\Delta n^2_{1/2}) \ln(1/T_{max})/\ln(2) \; . \tag{5}$$

Thus, it is necessary to know the difference $\Delta n_{1/2}$ between the refractive indices of the immersion liquid and of the glass grains for $T_{max}/2$ at constant temperature with sufficient precision. This problem, however, can be overcome by a different procedure: one determines the temperature coefficient $\mathrm{d}n_{fl}/\mathrm{d}\vartheta$ of the refractive index of the fluid (being much larger than that of the glass) and measures the spectral transmittance curve at constant wavelength (632.8 nm of the HeNe-laser, e.g.) as a function of the temperature. (The variation of the refractive index of the glass with the temperature is often neglected, since the temperature coefficients of inorganic glasses $\mathrm{d}n_{gl}/\mathrm{d}\vartheta$ are usually much smaller than those of liquids. If necessary, however, the variation of the refractive index of the glass with the temperature can be taken into account.) In this case, the difference of the refractive indices is not varied by changing the wavelength but by a variation of the temperature. This results in a spectral transmittance curve of the Christiansen filters as a function of the temperature. With the temperature ϑ_1 and ϑ_2, for which the transmittance is just half maximum,

$$|(\vartheta_1 - \vartheta_2)\, \mathrm{d}n_{fl}/\mathrm{d}\vartheta|^2 = (2\Delta n_{1/2})^2 \tag{6}$$

yielding from equation (5)

$$\sigma^2 = |(\vartheta_1 - \vartheta_2)\, \mathrm{d}n_{fl}/\mathrm{d}\vartheta|^2 \ln(1/T_{max})/(4\ln(2)) \; . \tag{7}$$

If the variation of the refractive index of the glass grains has to be taken into account, $\mathrm{d}n_{fl}/\mathrm{d}\vartheta$ has to be replaced in equation (7) by $(\mathrm{d}n_{fl}/\mathrm{d}\vartheta - \mathrm{d}n_{gl}/\mathrm{d}\vartheta)$.

The variation of the refractive index can also be achieved by applying pressure to the immersion liquid instead of varying the temperature [12]. In this case, the spectral transmittance curve is measured as a function of the pressure.

Figure 1 shows the theoretical internal transmittance of Christiansen filters as a function of the wavelength λ for different values of the parameter k^2 with the square of the standard deviation $\sigma^2 = 0$. With decreasing k^2 the spectral width of the transmittance curves becomes larger. This can also easily be seen in the argument of the exponential: if k^2 decreases, the rest $\pi^2 \lambda^{-2} \bar{d} z \Delta n^2$ must increase in order that the argument remains the same. Since π^2, $\bar{d}$, and z are constant and λ^2 does not vary considerably, this decrease of k^2 has to be compensated by an increase of Δn^2. According to Raman, the parameter k^2 is expected to characterize the shape of the glass grains if the packing density of the filling factor, i.e., the ratio between the volume occupied by the glass grains to the sum of the volume of the immersion liquid and the glass grains, remains constant. Experimentally, however, one observes that the width of the transmittance curves rather depends on the aperture angles (horizontal and vertical) of the beam used for the transmittance measurements [12] than on the shape of the grains and the packing density: large aperture angles cause broad spectral transmittance curves yielding small values of k^2, whereas small angles are responsible for small halfwidth yielding large values of k^2. This, however, is in contrast to the proper meaning of k^2 defined by Raman [2]. k^2 has been calculated for special cases only, such as spheres and cubes. Therefore, k^2 has to be determined in general from experimental spectral transmittance curves. k^2, however, determines the value of σ^2. This can easily be seen from equation (1). If k^2 is small, Δn^2 must be large in order that T decreases to fit a bell-shaped transmittance spectrum. At the same time, however, the influence of the inhomogeneity of the refractive index σ^2 can be seen from the transmittance curve only if σ^2 is in the order of Δn^2. Thus, according to equation (1), small values of σ^2 can be detected only if k^2 is large, whereas large σ^2 can be seen only if k^2 is small. For short, *the value of k^2 defines essentially the value of σ^2*. This has been confirmed by numerical calculations. Figure 2 shows the internal transmittance spectra from figure 1 modified by inhomogeneities of the refractive index, σ^2, which are necessary to decrease the maxima by an appreciable amount according to equation (1). If $\sigma^2 > 0$, the transmittance maxima are lower, whereas the halfwidth and consequently k^2 remain approximately constant. As has been mentioned already above, k^2 and thus the halfwidth of the transmittance curves depend sensitively on the aperture angles of the measuring beam, which can be changed arbitrarily depending on the experimental equipment. Depending on the aperture angle, however, the halfwidth entering equations (5) and (7) can vary by several orders of magnitude. As a consequence, the value of σ^2 characterizing the inhomogeneity of the refractive index can be adjusted experimentally at will using equation (1) for the evaluation.

3. Results of different authors

An arbitrary selection of data on the inhomogeneity of the refractive index of different glasses is summarized in table 1. All data have been obtained from the spectral transmittance of Christiansen filters using the evaluation method of Shelyubskii [3]. It is surprising that optical glasses show values of σ^2 in the order of some 10^{-9} and 10^{-6} depending on the year of investigation. Furthermore, the square of the mean deviation of the refractive index of optical glasses, σ^2, may be in the same order of magnitude as that of container glass, as can be seen in the first and the second line of the table. It is hard to believe that the homogeneity of container glass is of the same order as that of optical glass and that the homogeneity between optical glasses may differ that much. The explanation for these remarkable results is easily understood: the transmittance spectra of [10] have been obtained using an HeNe laser with rather small aperture angles (delivering necessarily small values for the homogeneity on the basis of equation (1)), whereas the other data correspond to experimental results using spectrometers with larger aperture angles. In fact, the data of σ^2 correlate with the aperture, as is expected according to the discussion above.

4. Critique, discussion, and conclusion

The results show very clearly that Shelyubskii's evaluation method of the spectral transmittance of Christiansen filters [3] does not provide useful data on the inhomogeneity of glasses. Shelyubskii's evaluation method is based on an extension of Raman's formula [2] on the spectral transmittance of Christiansen filters made by immersing glass grains into an index matching fluid. Since Raman's formula had already been questioned in a previous paper [1], it is not surprising that Shelyubskii's extension of that formula fails, too. The main reason is that in Raman's formula several contributions to the transmittance losses are neglected. Raman and Shelyubskii did not consider Fresnel's reflection losses, Rayleigh scattering and the change of the aperture angles due to refraction and diffraction.

Several other authors criticized the application of the Raman-Shelyubskii formula, too [6 to 9]. However, a clear statement of the reliability of Shelyubskii's evaluation method was missing until now. Varshneya, Loo, and Soules state "the failure of the Raman-Shelyubskii theory to fully describe the experiment" in [7]. They applied Monte Carlo calculations considering refraction and reflection to fit their transmittance data. In the same paper, however, the authors applied Shelyubskii's theory

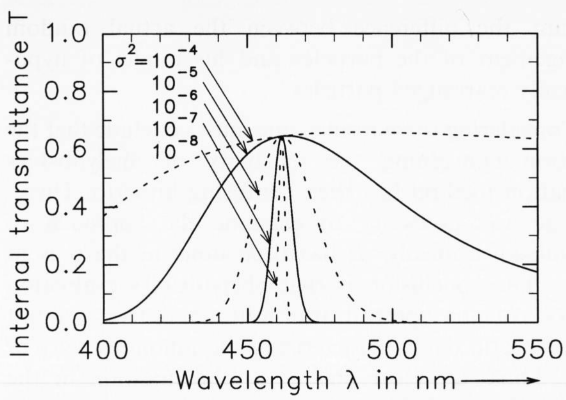

Figure 2. Theoretical internal transmittance of Christiansen filters made of inhomogeneous glass as a function of wavelength, λ, according to equation (1), i.e. the formula of Raman and Shelyubskii [3], for different values of k^2 and σ^2. Parameters: z = 5 mm, d = 0.19 mm; the data of the refractive indices are taken from [1]. σ^2 has been chosen in such a way that the transmittance maxima in figure 1 (where $\sigma^2 = 0$) are appreciably reduced.

Table 1. Mean square of the deviations of the refractive index of different glass types, σ^2, using Shelyubskii's evaluation technique of the spectral transmittance of Christiansen filters

type of glass	value of σ^2	year and reference
optical glass	$2.916 \cdot 10^{-9}$	1995 [10]
container glass	$7.225 \cdot 10^{-9}$	1995 [10]
container glass I	$6.76 \cdot 10^{-8}$	1995 [10]
container glass II	$2.44 \cdot 10^{-8}$	1995 [10]
float glass	$1.69 \cdot 10^{-8}$	1995 [10]
optical glasses	$(2.33-5.62) \cdot 10^{-6}$	1968 [5]
container glass	$(9.5-91) \cdot 10^{-8}$	1986 [9]
borosilicate glass (General Electric)	$(0.34-0.8) \cdot 10^{-6}$	1985 [7]

and concluded "that good reproducibility and a good sensitivity are obtained in measuring glass inhomogeneity by using the Shelyubskii wavelength scan method".

Aylward, Cable, and Wang criticized Shelyubskii's evaluation method in [9]; they even proposed a new formula (unfortunately without derivation). Finally, however, they concluded: "it is also clear that the calculated Shelyubskii variance is not the true variance of refractive index in glass but it remains a useful practical index". In an earlier paper, Afghan and Cable [6] came to a similar conclusion: "Although Shelyubskii's technique is very useful in practice it does not correctly predict the variance of the refractive index in the sample; a theory based on geometric optics is needed for this case".

Imagawa critically examined Shelyubskii's formula in [13]. The main result was that "a correction factor, β, was introduced into Shelyubskii's formula to take into account the difference between the actual random arrangement of the particles and his model of hypothetically rearranged particles".

Considering these results, one must conclude that the situation concerning the reliability of Shelyubskii's evaluation method has been confusing hitherto. Therefore, it was necessary to examine the approach of Shelyubskii critically, as has been done in the present paper. The conclusion is that Shelyubskii's evaluation method of the spectral transmittance curves cannot deliver useful data characterizing the inhomogeneity of glass. Thus, the clear answer to the question in the headline is: no. With a suitable new theory and using different evaluation procedures, however, it still seems to be possible to characterize the inhomogeneity of glasses from the internal spectral transmittance curves of Christiansen filters.

*

The author thanks M. Sc. Frank Richter for critical reading of the manuscript.

5. References

[1] Hoffmann, H.-J.; Steinhart, R.: Spectral transmittance of Christiansen filters – Experimental observations. Glastech. Ber. Glass. Sci. Technol. **71** (1998) no. 11, p. 319–326.

[2] Raman, C. V.: The theory of the Christiansen experiment. Proc. Indian. Acad. Sci. **A29** (1949) no. 5, p. 381–390.

[3] Shelyubskii V. I.: A new method for determining and controlling the homogeneity of glass. (Orig. Russ.) Steklo Keram. **17** (1960) no. 8, p. 17–22.

[4] Optical glass. Catalogue no. 10.000, 1992. Schott Glas, Mainz (Germany).

[5] Hilbig, G.; Eifert, U.; Ulrich, P.: Inhomogenitätsbestimmungen von Gläsern mittels Christiansen filter. Silikattechnik **19** (1968) no. 2, p. 48–50.

[6] Afghan, M.; Cable, M.: Estimation of the homogeneity of glass by the Christiansen filter method. J. Non-Cryst. Solids **38/39** (1980) p. 3–8.

[7] Varshneya, A. K.; Loo, M. C.; Soules, T. F.: Glass inhomogeneity measurement using the Shelyubskii method. J. Am. Ceram. Soc. **68** (1985) no. 7, p. 380–385.

[8] Varshneya, A. K.: Glass inhomogeneity measurement by Shelyubskii technique – A criticism of Raman's Christiansen filter theory. In: XIV Intl. Congr. On Glass, New Delhi 1986. Collected papers. Vol. II. Calcutta: Indian Ceram. Soc. 1986. p. 271–279.

[9] Aylward, N. H.; Cable, M.; Wang, S. S.: Some practical problems in estimating the homogeneity of glass by the Christiansen filter method. XIV Intl. Congr. On Glass, New Delhi, India, Collected papers. Vol. II. Calcutta: Indian Ceram. Soc. 1986. p. 281–287.

[10] Tenzler, T.; Frischat, G. H.: Application of the Christiansen-Shelyubskii method to determine homogeneity and the refractive index of industrial glasses. Glastech. Ber. Glass Sci. Technol. **68** (1995) no. 12, p. 381–388.

[11] Janke, A.; Frischat, G. H.: Improved homogeneity of various glasses by gas film levitation. Glastech. Ber. Glass Sci. Technol. **71** (1998) no. 7, p. 193–198.

[12] Inoue, S.; Yamane, M.; Serizawa, T.: An apparatus for precise measurement of glass homogeneity by Shelyubskii's method. Am. Ceram. Soc. Bull. **63** (1984) no. 11, p. 1412–1415.

[13] Imagawa, H.: Quantitative measurements of glass inhomogeneity by the Shelyubskii method. Glass Technol. **14** (1973) no. 3, p. 85–88.

0499P001

Address of the author:

H.-J. Hoffmann
Institut für Nichtmetallische Werkstoffe
Glaswerkstoffe
Technische Universität, Berlin
Englische Straße 20
D-10587 Berlin