Optica Applicata, Vol. XXIV, No. 1–2, 1994

Effective optical constants and scattering in porous glasses. Theoretical evaluation

S. A. Kuchinsky

S. I. Vavilov State Optical Institute, St. Petersburg, 199034, Russia.

Models of porous glass microheterogeneous structure for effective optical constants and light scattering evaluation have been suggested. Taking into account collective effect on light scattering, analytical expressions for the effective optical constants and extinction coefficient of porous glass prepared by etching have been derived.

1. Introduction

Optical properties of porous glass (PGL) were investigated in many papers [1]–[9]. In paper [1], the waveguide effect was found. In papers [2]–[4], light attenuation and scattering were investigated experimentally. Optical anisotropy was studied in [5], [6]. PGL impregnated with liquid crystals was considered as a perspective medium for optical information storage in [7]. PGL impregnated with photosensitive substrates were studied in [8] as a recording material for 3-D holography.

Theoretical treatment of all the problems mentioned above is to be based on calculations of the effective optical constants. An attempt at calculating of the effective complex refractive index was undertaken in [9]. The present paper describes further development of the approach to the effective optical constants calculations suggested in [9].

2. Model of PGL structure and approach to the effective optical constants calculations

It is known that microporous glass consists of hard silica frame whose cavities contain the secondary silica having a network of communicating micropores. The free volume of PGL can be filled with different compositions. For example, in holography applications (the case of our practical interest) micropores contain photosensitive substrate filling a part of the free volume, the rest of the free volume being filled with the filler introduced to suppress scattering. Besides, there are regular inhomogeneities with a period much greater than the size of silica frame cavities. Thus impregnated PGL is a complex heterogeneous medium with different characteristic sizes of inhomogeneities:

1. The content of micropores is, generally, a two-phase system with inhomogeneities of a molecluar size.

2. The characteristic size of micropores in the secondary silica that fill the cavities of silica frame is about several nm.

3. The characteristic size of silica frame cavities is about several tens of nm.

4. The period of regular inhomogeneities is about several μm.

The effective optical constants (real and imaginary parts of the complex refractive index $N = n + ik$) depend on the structure parameters (statistical parameters characterizing the pores size, the pores shape and their relative positions) and optical constants of all components of the heterogeneous system under consideration.

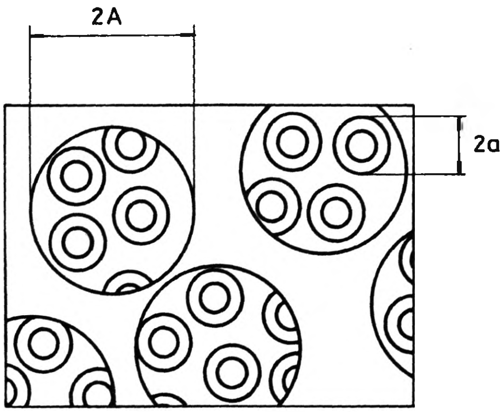

Fig. 1. Model of impregnated microporous glass for calculations of the effective optical constants. $2A$ – size of silica frame cavities, $2a$ – size of micropores

The aim of the present work is determination of the complex refractive index, whose real part determines the phase, and the imaginary part determines the decrease of amplitude of light wave. In the present paper, we start an investigation of the dependencies of the effective optical constants of impregnated PGL with consideration of a simple structural model allowing theoretical treatment (Fig. 1). In this model, the cavities of silica frame are represented by a system of identical nonoverlapping spheres of radius A. The structure of the secondary silica inside the frame cavities is modelled in the same way, a being the micropore radius. The micropore volume is assumed to be filled with two substances forming a shell structure. First, the phase composition inside micropores is replaced by an effective homogeneous medium characterized by an effective refractive index n_e. Later, the secondary silica is replaced by an effective medium with effective optical constants. Finally, the effective optical constants of the system as a whole are found. The next Section presents equations for the effective optical constants at each stage of the calculation procedure shown in Fig. 1.

3. Equations for the effective optical constants

Let n_1 and n_2 be the refractive indices of inner and outer parts of the shell structure formed in micropores, n_m is the refractive index of silica. The effective refractive index n_a of the effective medium inside micropores is defined by the conditions that polarizability of homogeneous spherical particle (α_{sph}) should be equal to that of shell system (α_{shell}). In accordance with [10]:

$$\alpha_{sph} = a^3 \frac{n_a - n_m}{n_a + 2n_m}, \tag{1}$$

$$\alpha_{shel} = a^3 \frac{(n_2^2-1)(n_1^2+2n_2^2)+q^3(2n_2^2+1)(n_1^2-n_2^2)}{(n_2^2+2)(n_1^2+2n_2^2)+q^3(2n_2^2-2)(n_1^2-n_2^2)} \tag{2}$$

where q is the ratio of inner to outer radius of a shell. Condition $\alpha_{sph} = \alpha_{shell}$ yields

$$n_a = n_2 \left(\frac{n_1^2+2n_2^2+2(1-f_s)(n_1^2-n_2^2)}{n_1^2+2n_2^2-(1-f_s)(n_1^2-n_2^2)} \right)^{1/2} \tag{3}$$

where f_s is the volume fraction of a shell.

The problem of effective optical constants calculation for heterogeneous system inside silica frame cavities is reduced to that for a system of identical nonoverlapping particles. For the case, where the particle size is much less than wavelength this problem was solved in [11]. The separation of real and imaginary parts of the effective propagation constants obtained in [11], in the quasicrystal approximation, leads to the following expressions for the effective refractive index n_e and extinction coefficient γ_e:

$$n_e = n_m \left(\frac{(1+2f)n^2+2(1-f)n_m^2}{(1-f)n^2+(2+f)n_m^2} \right)^2, \tag{4}$$

$$\gamma_e = 2k\frac{n_m}{n_e} f\rho^3 \left(\frac{n^2-n_m^2}{(1-f)n^2+(2+f)n_m^2} \right)^2 \frac{(1-f)^4}{(1+2f)^2} + \frac{n}{n_e}\gamma f \left(\frac{3n_m^2}{(1-f)n^2+(2+f)n_m^2} \right)^2 \tag{5}$$

where $k = 2\pi n_m/\lambda$ is the constant of light propagation in the matrix, f is the relative volume (the volume fraction) occupied by particles in the medium, and $\rho = kR$ is the diffraction parameter.

Calculating the effective optical constants n_s and γ_s for the system as a whole, Eqs. (4) and (5) are used for determining the effective parameters n_A and γ_A for the cavities in the silica frame. This is proceeded by substitution into Eqs. (4) and (5) and n_a for n, the volume fraction of micropores f_a for f, and radius of pores in the secondary silica for R. As a result we have:

$$n_s = n_m \left(\frac{(1+2F)n_a^2+2(1-F)n_m^2}{(1-F)n_a^2+(2+F)n_m^2} \right)^{1/2}, \tag{6}$$

$$\gamma_s = 2kf_A \frac{n_m}{n_s} \left[\rho_A^3 \left(\frac{f_a(n_a^2-n_m^2)}{(1-F)n_a^2+(2+F)n_m^2} \right)^2 \frac{(1-f_A)^4}{(1+2f_A)^2} + \rho_a^3 f_a \left(\frac{(1-f_a)n_a^2+(2+f_a)n_m^2}{(1-F)n_a^2+(2+F)n_m^2} \right)^2 \frac{n_a^2-n_m^2}{(1-f_a)n_a^2+(2+f_a)n_m^2} \frac{2(1-f_a)^4}{(1+2f_a)^2} \right] \tag{7}$$

where $F = f_a f_A$ is volume fraction of micropores in porous glass (the porosity).

Note that Equation (6) is equivalent to Eq. (4), when $f = F$ and $n_a = n$. In other words, the effective refractive index of the heterogeneous system in question does not depend on the distribution of micropores in the sample. It is determined only by the overall volume of pores. The statement is true when the refractive index of the secondary silica is equal to that of the hard silica frame.

Now, let us analyse the extinction coefficient γ_s. The first term in Eq. (7) describes the scattering by the cavities of the silica frame of radius A, whereas the second term describes the scattering by micropores of the secondary silica of radius a.

For real values of the parameters of the system under study, the ratio of these two terms is about $(A/a)^3$. The second term in Eq. (7) can be disregarded because the radii A and a of respective inhomogeneities differ by an order of magnitude.

Thus, the light scattering of the system is chiefly determined by the size of the silica frame cavities, their volume fraction f_A, the difference between the refractive indices of the content of micropores and the silica frame, and the volume fraction f_a of micropores in the secondary silica. It is essential that the dependence of γ_s on f_a is quadratic.

4. Results and discussion

Equations (3), (6) and (7) allow investigating dependencies of the effective refractive index and extinction coefficient due to scattering on the volume fraction of pores and impregnated substances as well as the optical constants of all components of the system. Such investigation for photosensitive composites based on PGL for holography has been performed [8]. In the present paper, some general features of the dependencies of effective optical constants of PGL on its sutructure and optical properties of its components are discussed.

As it can be seen from Eq. (6), the effective refractive index of PGL (n_s) impregnated with medium with the refractive index n_a is not additive value. In other words, the dependence $n_s(n_a, F)$ in Eq. (6) is not linear. This nonlinearity is essential for not very small different refractive indices n_a and n_m. Really, expanding Eq. (6) in series of $(n_a - n_m)$ we have

$$n_s = Fn_a + (1-F)n_m - \frac{F(1-F)}{6[Fn_a + (1-F)n_m]}(n_a - n_m)^2 + O[(n_a - n_m)^2]. \tag{8}$$

It should be noted that Equation (6) is valid for a particular structure model used in this paper. On the contrary, Eq. (8) is valid for any structural model. This statement was proved in [12] using the theory of effective dielectric constant bounds.

Now, let us discuss scattering. As a rule, in experimental work microporous glass structure is characterized by the porosity and average pore radius. At the same time, the extinction coefficient (Eq. (7)) depends on not only pore radius a and the porosity $F = f_a f_A$ but, in the main, on the radius of silica frame cavities, and both the volume fraction of micropores (f_a) in the secondary silica and the volume fraction of

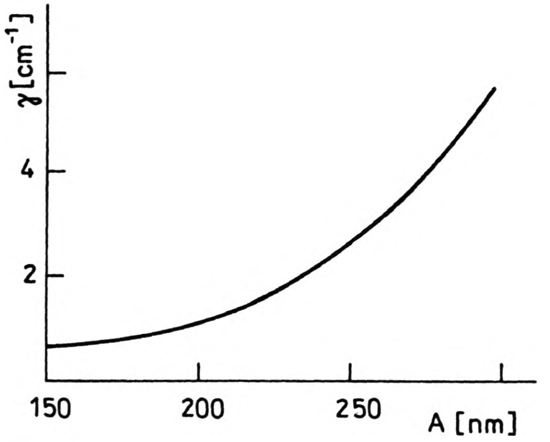

Fig. 2. Dependence of the extinction coefficient γ of micropores glass on the radius of silica frame cavities A. $f_A = 0.44$, $f_s = 0.68$, the porosity $F = f_s f_A = 0.3$. The micropores radius $a = 30$ Å

the silica frame cavities. Figure 2 shows that the extinction coefficient of micropores glasses with the same porosity and the micropore radius can be quite different.

The influence of the amount of secondary silica on light scattering of PGL can be revealed by comparison between the transparency before and after complete removal of the secondary silica from microporous glass sample. (In the latter case, the porous glass is a macroporous one). The results of the extinction coefficient calculations are presented in the Table. One can see that complete removal of the secondary silica leads to an increase of the extinction coefficient several times being in agreement with the experiment [5]. Note that the simplest Rayleigh equation [10] which does not take into account collective effects accomplishing light scattering in PGL predicts much greater increase of scattering.

Table. The extinction coefficient of micro-PGL and macro-PGL

PGL	Structural parameters				Extinction coefficient (cm^{-1}), $\lambda = 540$ nm	
	f_s	f_A	a [Å]	A [Å]	Our calculation	Rayleigh equation
Micro-PGL	0.68	0.44	35	200	1.67	1.01
Macro-PGL	1	0.44	—	200	3.52	279

Another interesting fact to be pointed out is a possibility to decrease scattering by formation of solid shells on the inner pores surfaces. Within the structural model assumed in the present paper (Fig. 1), the extinction coefficient is equal to zero for $n_1 = 1$ and n_2 satisfying the condition

$$n_m = n_2 \frac{1+2n_2^2+2(1-f_s)(1-n_2^2)}{1+2n_2^2-(1-f_s)(1-n_2^2)}. \tag{9}$$

In conclusion, it shoul be underlined that the results obtained in this paper are rather qualitative ones because the structural model used is a very rough reflection of the real structure. Considering more realistic models (in particular, cylindrical or spheroidal channels instead of the spherical cavities) is the subject of our further work.

Acknowledgements – The author is grateful to Dr A. Alekseev–Popov, M. Khazova and Professor V. Sukhanov for interesting and helpful discussion.

References

[1] ALTSHULER G. B., *et al.*, Opt. Spektrosk. (in Russian) 65 (1988), 995.
[2] BEGER B. N., STEPANOV V. E., Opt. Spektrosk. (in Russian) 69 (1990), 412.
[3] ROSKOVA G. P., MOROZOVA E. V., BAKHANOV V. A., Fiz. Khim. Stekla (in Russian) 17 (1991), 623.
[4] ROSKOVA G. P., TSEKHOMSKAYA T. S., BAKHANOV V. A., Fiz. Khim. Stekla (in Russian) 15 (1989), 874.
[5] BURKAT T. M., KOSTYUK G. K., YAKOVLEV E. B., Fiz. Khim. Stekla (in Russian) 17 (1991), 781.
[6] ALTSHULER G. B., *et al.*, Fiz. Khim. Stekla (in Russian) 17 (1991), 791.
[7] REZNIKOV YU. A., YAROSCHUK O. V., Ukr. Phys. J. (in Russian) 36 (1991), 1062.
[8] KUCHINSKY S. A., SUKHANOV V. I., KHAZOVA M. V., Laser Physics 3 (1993), 1114.
[9] KUCHINSKY S. A., *et al.*, Opt. Spectrosc. 70 (1991), 150.
[10] TSANG L., KONG J., J. Appl. Opt. 51 (1980), 3465.
[11] VAN DE HULST H. C., *Light Scattering by Small Particles*, New York 1957.
[12] KUCHINSKY S. A., POTEKHINA I. YU., Fiz. Khim. Stekla (in Russian) 15 (1989), 272.

Received June 6, 1994