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Optical properties and structure of porous glasses

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The results of measurements concerning spectral dependences of transmission and reflection coefficients both for porous and two-phase glasses are presented. Relative estimations have been performed for transmission and reflection coefficients of examined samples. Optical characteristics, such as the dispersion of refractive index and absorption coefficient, have been found for porous glasses. Porosity of the material and the sizes of micropores have been determined from the optical characteristics of glasses with the assumption of identity and uniformity of pores.

Keywords: porous glass, photometry measurement, spectral dependence, transmission, reflection, scattering, refractive index, porosity, size of microstructures.

1. Introduction

Porous glasses (PGs), unique technological materials, find nowadays their application in quantum electronics [1], optics [2], [3], instrument industry [4]–[7] and analytical engineering [8]. Technologies of PGs fabrication allow us to reproduce structures and to design their optical, mechanical and sorption properties [9]–[13].

PGs represent complex heterogeneous media with various distinctions between inhomogeneities such as the scale of the cavities of a basic silica skeleton, the size of micropores, the spaces between globules of secondary silica, *etc.* Heterogeneity of each type contributes to the properties of a sample.

Papers devoted to the study of optical properties of PGs are based on certain models of PG structure, for example, on the assumption of the existence of lamellar sedimentations of silica gel, oriented along the planes parallel to the edges of samples [14], [15], and heterogeneities of silica gel in the form of rods, oriented perpendicularly to the biggest edges of the sample [1], [12], [16].

Optical effects, such as anomalous propagation of light through wave-guides formed within PGs medium [14], [17], [18], have attracted our attention. In this paper we present optical data measured and analyzed for PG samples produced by the leaching technique [12].

2. Samples, equipment and measurements methods

PG samples were fabricated from two-phase glasses: PG1, PG2, PG10 from glass 8B and PG9 from glass NFF. Samples of a rectangular form sizes of 15×15 mm^2 and of 2 mm thickness were used for measurements.

Spectral characteristic of the samples were measured for transmission and reflection light modes with a HITACHI U3410 spectrophotometer (Japan) operating in the 200–850 nm spectral range. 5° Specular Reflectance attachment N 210-2133 (Hitachi) was applied for the measurements of samples. Polarization properties were measured using the spectral transmission coefficient of polarized light in the spectral

Table 1. Characteristics of two-phase and porous glasses.

Sample	Characteristics	Note
Glass NFF	$D_{macropores}$ = 25–30 nm*, relative volume of unstable phase ~ 65%	* Transmission electronic microscopy (method of cellulose-coal retorts)
PG9	$D_{macropores}$ = 25–33 nm*	
	Micro pores: R_1 = 6.5 nm; R_2 = 10.5 nm (~7% from total volume) V = 0.23 sm^3/sm^3 (23%) S_{spec} = 35 m^2/g (porosity ~ 30%*)	Mercury porosimetry
Glass 8B	$D_{macropores}$ = 25–45 nm*, relative volume of unstable phase ~ 55%	
PG1	$D_{macropores}$ = 25–50 nm*,	
	Micropores: R = 2.5 nm (H_2O) – 1.7 nm (N_2) V = 0.25 sm^3/sm^3 (H_2O); 0.28 sm^3/sm^3 (N_2) S_{spec} = 269 m^2/g	Adsorption steam of water at 18 °C
PG2	$D_{macropores}$ = 25–45 nm*	
	Micropores: R = 3.3 nm V = 0.27 sm^3/sm^3 (27%) (porosity ~ 30%*)	Adsorption steam of water at 18 °C
PG10	$D_{macropores}$ = 37–43 nm* $D_{Si\text{-}particle}$ = 5.5–7 nm*	
	Micropores: R = 1.4 nm V = 0.25 sm^3/sm^3 (25%) S_{spec} = 322 m^2/g	Adsorption steam of water at 18 °C

range of 400–750 nm with the attachment Polarizer Accessory N 210-2130 (Hitachi). The speed of spectral measurements was equal to 120 nm/min with 2 mm spectral width. The measurements were performed for the samples annealed for 2–3 hours at 120 °C after cooling to the room temperature 25–30 °C. Some characteristics of the samples, which were obtained using transmission electronic microscopy, are also collected in Tab. 1.

3. Estimations and characteristics

Spectral dependences of light transmission of PG provide valuable information about the samples. While the absorption coefficient of the material is low, the extinction of light stream depends just on radiation scattering by porous structures. Different ways of light scattering may be observed, depending on size- and form-distribution functions of light scatterers (inhomogeneities). The Rayleigh scattering of light takes place when the sizes of phase inhomogeneities are much smaller than radiation wavelength, as described in [1], [3], [19]. In other cases, when inhomogeneities of bigger sizes are presented, the light scattering follows more complex dependences [10], [20]. Macropores and the microparticles embedded in pores also control the effects of the interaction of light with these structures. The extinction of light stream depends on the properties of scattering medium in a more complex way when the density of scatterers is high, as compared to the case of their low density. Here we use approximate dependences for the estimation of an extinction factor for such media [20].

3.1. Transmission PG

The extinction of light flow through a medium containing particles depends on the absorption and scattering on these particles. It is known that an extinction spectrum depends on the radiation wavelength as $1/\lambda$, when the sizes of these particles are small and absorption is dominant. When the scattering process becomes dominant, the dependence is proportional to $1/\lambda^4$ [21].

Let us assume that the extinction of light follows the form

$$\lg\frac{1}{T} = D_\lambda = C_1\lambda^\beta. \tag{1}$$

Taking the logarithm, Eq. (1) turns to

$$\ln D_\lambda = C_2 + \beta\ln\lambda. \tag{2}$$

Linearity of the Eq. (2) confirms the fact that the sizes of particles are rather small. Figure 1 shows that the linear dependence takes place only for PG9; more complex dependences are observed for other cases, especially for PG10. For PG9 factor $\beta > 4$, this is probably caused by more complex processes of scattering and absorption. An explanation of the laws of higher order requires an application of more sophisticated models of PGs structure.

It is also seen that the linear approximation of the dependence $\ln(D_\lambda)$ is valid for the spectral range 340–670 nm for all samples of PGs with high accuracy (Fig. 1 and

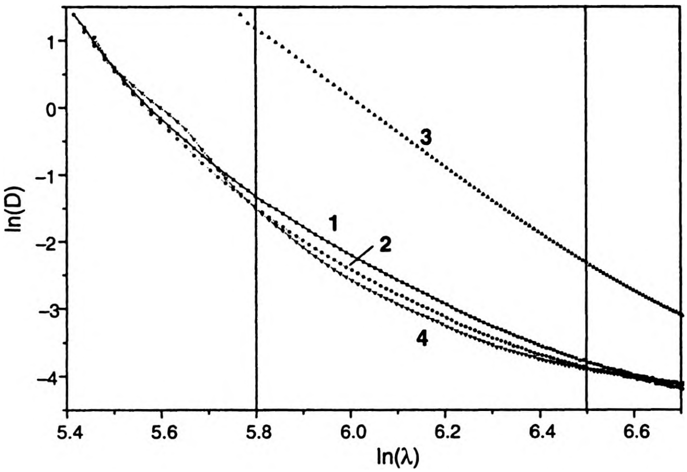

Fig. 1. Weakening of light stream in PG1 (curve 1), PG2 (curve 2), PG9 (curve 3), PG10 (curve 4).

Table 2. Values of coefficients C_2 and β at linear approximation.

Sample	C_2	β
PG1	19.77±0.33	−(3.64±0.05)
PG2	19.09±0.44	−(3.55±0.07)
PG9	30.09±0.11	−(4.99±0.02)
PG10	19.67±0.65	−(3.66±0.11)

Tab. 2). The Rayleigh scattering becomes dominant for this spectrum range for the samples PG1, PG2 and PG10 (factor β is about 4).

Spectra of relative transmission T_{PG}/T_{BASE} show the contribution of heterogeneities, originating in PG, to the overall optical properties of the material. The distinction exists between similar dependences for the samples PG1 and PG2 and the dependence for PG9 (Fig. 2).

We believe that the modification of optical properties of samples is caused by formation of microstructure. It is possible for different types, which follows from spectral dependences. These microstructures are raised a relative transmission coefficient for PG10 in the interval from 505 nm and more, and PG1 – from 565 nm and PG2 – from 530 nm. The same structures are responsible for the absorption peak with maxima at 280 nm for PG 10, 290 nm for PG1 and PG2.

The relative transmissions for PG1, PG2 and PG10, in the above mentioned spectral range, exceed a little the transmission of the initial glass (for about 3–4%). This fact can be explained in terms of the formation of waveguide-type macrostructures responsible for the localization of the light stream.

The first derivatives of the transmission dependence of the samples, measured at light transmission of air as a reference, are used for the detailed analysis of spectral

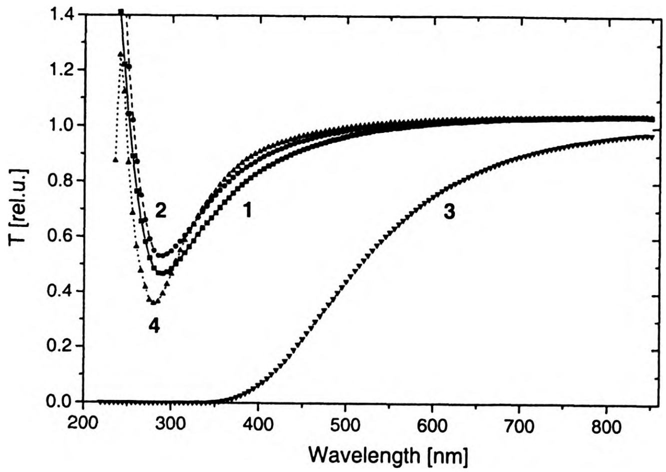

Fig. 2. Relative transmission of PG: PG1/glass 8B (curve 1), PG2/glass 8B (curve 2), PG9/NFF (curve 3), PG10/glass 8B (curve 4).

dependences (Fig. 3). The derivative allows us to reveal sites of the maximal change in the transmission through the visualization of inflection points.

The dependences for NFF glass and 8B glass are similar, but there is a difference in the position of maxima: for NFF $\lambda_{max} = 285$ nm, for glass 8B $\lambda_{max} = 275$ nm, the peaks have symmetric increase and decrease with identical widths. Dependences for PG demonstrate asymmetrical and wider peaks as compared to two-phase glasses. The spectral positions of peak maximums are also different: for PG1 and PG2 $\lambda_{max} = 290$ nm, for PG9 $\lambda_{max} = 475$nm, PG10 $\lambda_{max} = 300$ nm. The derivatives of

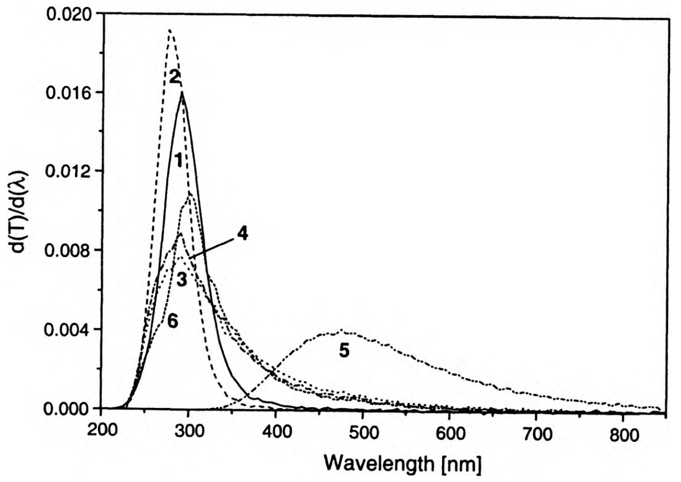

Fig. 3. Derivatives of the transmission of porous and two-phase glasses: glass 8B (curve 1), NFF (curve 2), PG1 (curve 3), PG2 (curve 4), PG9 (curve 5), PG10 (curve 6).

transmission $dT/d\lambda$ for PG1 and PG2 coincide (approximately identical width of the spectra, the shape of the curves, the position of the maxima). It is possible to assume that the structure of these samples is similar. The derivative of PG10 transmission has a more complex shape. Probably, the resulting spectrum could be presented as a superposition of two or more spectra and various models may be applied for an interpretation of the experimental data.

Measurements of polarization properties of PG1 and PG2 were carried out in our previous papers. The polarization properties are maximal for the sample PG1 [22], [23]. These data confirm the presence of the effect of birefringence of PG that has been found earlier [9], [18]. The similar measurements have shown that the glasses PG9 and PG10 have no pronounced polarizing properties. The assumption of the absence of regular microstructures interacting with polarizing light (or the assumption about the chaotic character of an arrangement of similar structures in the volume of the sample) may be used as a hypothesis for these samples.

3.2. Reflection of PG

Measured samples demonstrate mirror and diffuse components of the reflection. In some cases the diffuse component dominantes mirror components in porous glasses. All the samples were measured in comparison with the sample of glass (MC20), and then relative reflections (concerning initial two-phase glass) were obtained (Fig. 4).

Analyzing the dependences, it is possible to distinguish three groups: the first group includes the samples PG1 and PG10, the second – PG2, and the third one – PG9. The first group is characterized by the presence of narrow areas of a decreased reflection coefficient with minima at 305 nm (PG1) and 300 nm (PG10). The dependence for PG2 within the range of 200–300 nm repeats the dependence for PG1,

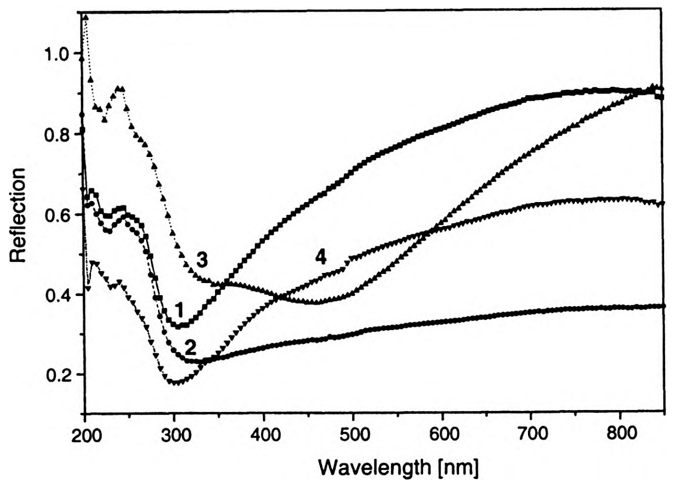

Fig. 4. Relative reflection PG: PG1/glass 8B (curve 1), PG2/glass 8B (curve 2), PG9/NFF (curve 3), PG10/glass 8B (curve 4).

but the minimum is shifted to 330 nm, and an insignificant increase in reflective ability of the sample is observed. The sample PG9 has a wide area of low reflection with a minimum at 460 nm.

3.3. Optical characteristics

Assuming homogeneous structure, lack of scattering and absorption for the samples when the coefficient $T > 90\%$, the average value of the refractive index n_e can be found by applying the formula for a thin layer to the experimental data [24]. This approximation becomes valid for thin two-phase glasses. To take into account optical absorption of the sample, a more complicated procedure should be used for the estimation of n_e. This procedure requires measurements of both transmission and

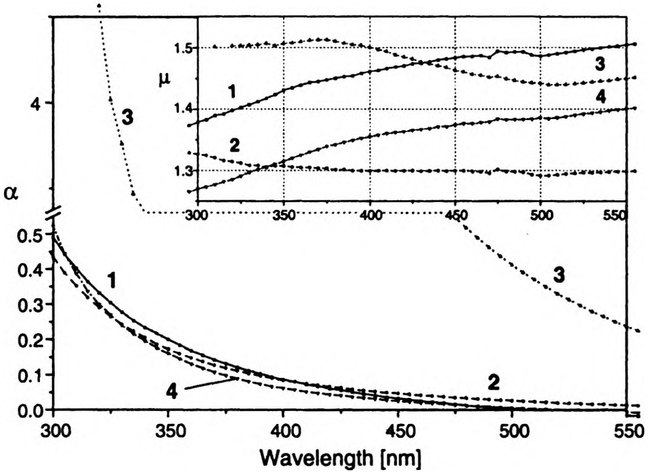

Fig. 5. Refractive index μ and absorption coefficient α for: PG1 (curve 1), PG2 (curve 2), PG9 (curve 3), PG10 (curve 4).

reflection spectra of the sample [25]. In this case the estimation of the absorption coefficient α, the imaginary part of the complex χ and the real part μ of the refractive index may be evaluated. Generally, the estimation error depends on the measurement error and the presence of scattering effects. Figure 5 shows the results of estimations of coefficients μ and α.

3.4. Estimations: porosity of samples and sizes of microstructures

For the effective refractive index of a porous layer for small values $(n-1)$ and lack of absorption the following formula is valid [26]:

$$n_{\text{eff}} = n\left[1 - \frac{NV(n^2-1)}{2}\frac{}{n^2} - i\,\frac{N2(\pi V)^2(n^2-1)^2}{3\lambda_0^3 n}\right] \tag{3}$$

where V – volume of the scattering pore, N – amount of pores in the unit of volume.

Table 3. Estimation of the sizes of microstructures and *NV* of samples.

Parameter	Sample	Estimation for 450 nm	Estimation for 500 nm
D [nm]	PG1	4.09	2.19
	PG2	3.47	3.38
	PG9	12.5	11.5
	PG10	3.55	2.33
NV	PG1	0.266	0.221
	PG2	0.637	0.624
	PG9	0.252	0.283
	PG10	0.752	0.623

We shall use this formula for estimations of product *NV* and sizes of microstructures (pores). The calculated values are shown in Tab. 3. For the estimation we have also neglected the effects of light localization within wave-guide structures.

4. Conclusions

Inhomogeneities of the PG control effects such as "wave-guide" (coherent light scattering) and non-coherent light scattering were observed in the course of the spectral measurements.

The Rayleigh scattering is observed among other effects in the spectral range of 340–670 nm for PG1, PG2 and PG10 samples. It is the evidence of the presence in the material scatterers with sizes less than the wavelength of the measurement. For a certain spectral range, the samples PG1, PG2 and PG10 showed transmission coefficients, higher than the initial two-phase glass–glass 8B, which probably results from the presence of macrostructures with large sizes, like "wave-guides", localizing and redistributing the radiation. The sizes of macrostructures can be evaluated using the model of a single-mode wave guide [22], [23]. Thus, the technology of PG fabrication provides the opportunity to increase PG transmission in a certain spectral range and to decrease it within another one. The spectral dependences of the first derivative can be used for an additional characterization of PG transmission spectra. These dependences allow us to obtain more information regarding optical properties of the samples. A single narrow peak with a maximum at 275 nm (glass 8B) and at 285 nm (glass NFF) was observed for two-phase glasses. The similar peaks were revealed for porous glasses demonstrating some widening (100–120 nm for PG1, PG2 and PG10; 180 nm for PG9) and a shift towards the long wavelength range (290 nm for PG1 and PG2; 300 nm for PG10; 475 nm for PG9).

The technique of fabricating PG allows us to design media that have optical activity. The samples PG1 and PG2 have pronounced polarizing properties.

The spectral dependences of reflection and transmission coefficients for the samples measured were used to determine such optical characteristics as a refractive index and absorption coefficient.

The approximate estimations of material porosity and of volume fraction of micropores could be applied for modeling of a simple porous medium. Such a hypothetic medium consists of identical and homogeneous pores with sizes and distances between them larger than the wavelength of radiation. The correlation of the estimations (Tab. 3) with the experimental results (Tab. 1) is the evidenc of the correctness of this approach.

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