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Spectral characteristics and structure of porous glasses

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The paper presents a method for the size estimation of scattering structures in porous glasses, being based on measurements of both the sample reflection and transmission. Analysis of the transmission spectra allows us to estimate the contribution of absorption and scattering to light extinction and to choose a wave range where the characteristics of a medium can be determined by means of simple and effective models. Optical characteristics of the highly light scattering samples can be obtained with use of the Gurevich–Kubelka–Munk method.

Keywords: porous glass, optical characteristics, Rayleigh scattering, refractive index, absorption, porosity, Gurevich–Kubelka–Munk formulae.

1. Introduction

Porous glasses (PG) are widely used in various fields of science and technology due to their unique properties [1–6]. The current technology makes it possible to produce porous structures with specific properties [7–9] which enable successful PG application in the state-of-the-art instrumentation and analytical systems. In order to use the PG in optical instruments, devices and sensors, one should know the optical characteristics and physical/chemical properties of porous structures. It seems appropriate to study the porous glasses with use of the optical spectroscopy techniques and to find correlation between optical characteristics of PG and characteristics of the structure inhomogeneities [10–12].

The purpose of this work is to develop a combined approach to estimation of scattering structure sizes in porous glasses using the spectrophotometric data. One of the tasks is to determine spectral ranges, where fairly simple and adequate models are applicable.

2. Experimental

Two-phase (8B and NK) and porous (PG2 and PG12) glass samples in the form of rectangular (15×15 mm) plates of 2 and 4 mm in thickness were studied. The two-phase glasses DV1SH and porous glasses DV1SH-2 and DV1SH-3 of 1 mm in thickness were also investigated. The transmission and reflection spectra of the samples were measured on the HITACHI U3410 spectrophotometer (Japan) in the 250 to 800 nm wave range. The mirror and diffuse reflection spectra were measured with reference to standard samples and scaled with regard to standard reflection. The spectrum scanning speed was 120 nm/min, with a spectral slit width of 2 nm.

The glass transmission spectra contain integrated information on the sample and its structure, absorption of the material, reflection and scattering of the light flux from the intermediate interface and structure inhomogeneities. When the light scattering is essential, the model used should take into account the light absorption and scattering. The best understood are the cases of Rayleigh scattering. The presence of large inhomogeneities in PG leads to diffraction scattering and Mie scattering. The real samples contain both small and large inhomogeneities, which complicates the light scattering pattern.

The light extinction in a particulate medium is caused by the light absorption and scattering from particles. In the case of small particles, when absorption dominates, the extinction spectrum varies as $1/\lambda$ ($Q_{\mathrm{abs}} \sim 1/\lambda$). If Rayleigh scattering prevails, the extinction spectrum varies as $1/\lambda^4$ ($Q_{\mathrm{sca}} \sim 1/\lambda^4$).

The light flux extinction can be expressed as $\log(1/T) = D_\lambda = C_1\lambda^\beta$ and then as $\ln(D_\lambda) = C_2 + \beta\ln(\lambda)$. The linearity and respective coefficients β prove the presence of scattering particles. Such an approach is useful in defining relationships not only between the absorption and Reyleigh scattering, but other types of light scattering as

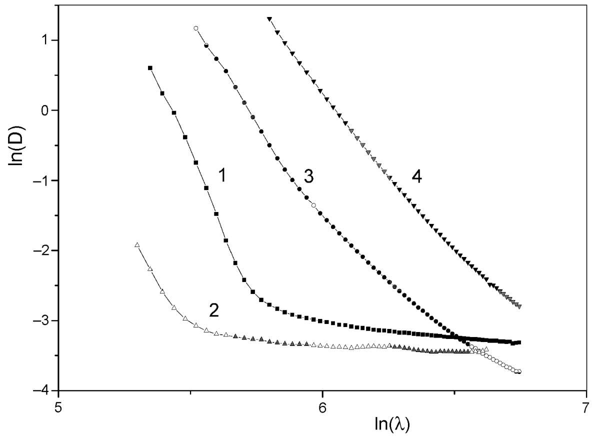

Fig. 1. Spectral dependences of ln(D) function for two-phase (curve 1 – 8B, curve 2 – NK) and porous (curve 3 – PG2, curve 4 – PG12) glasses.

well. Using straight line approximations, one can define the spectral ranges optimal for a certain model.

The relationship for the glass 8B (Fig. 1) can be interpolated by two straight lines. In the long wave region, the value $\beta < 1$ suggests that in this region the absorption is predominant. Spectral dependence for NK (Fig. 1) can be interpolated by two straight lines. The low value of β in the long-wave measurement region for two-phase glasses points to the low level of absorption and the absence of scattering. Porous glasses PG2 and PG12 exhibit almost the linear dependences over the entire range, with $\beta = 3.81$ (245–800 nm) for PG2 and $\beta = 4.29$ (340–800 nm) for PG12. For these glasses, one can assume the predominant role of the Rayleigh light scattering and use the earlier proposed method to determine structure characteristics [12].

Thus, it is possible for the porous glasses to find a spectral range where the light scattering predominates and to determine characteristics of the microstructures using the simple models and approximate solutions [12, 13]. On the other hand, the values obtained for β point to complex absorption and scattering processes in glasses.

3. Estimates and characteristics

The refractive index for the two-phase and porous glasses with low absorption and scattering (transmission $T \geq 90\%$) can be estimated from the simple formulae for thin layers. However, the light scattering makes it necessary to measure transmission T and reflection R and apply more complicated formulae [14]:

$$r_0 = \frac{-\left(T^2 - R^2 + 2R + 1\right) \pm \sqrt{\left(T^2 - R^2 + 2R + 1\right)^2 + 4R(R-2)}}{2(R-2)},$$

$$k = -\frac{1}{2l} \ln \frac{r_0 - R}{r_0\left[r_0(2-R) - 1\right]},$$

$$n = \frac{1 + r_0 + \sqrt{4r_0 - (1-r_0)^2 k_1^2}}{1 - r_0}$$

where $k_1 = k\lambda/4\pi$, l is the sample thickness, r_0 is the coefficient of reflection from the intermediate interface, k is the absorption coefficient, n is the refractive index.

These formulae are applicable when $k < 10^3$ cm^{-1}. The attained optical constant estimation error depends on the R and T measurement accuracy.

The absorption coefficient spectra and reflective index dispersion of the glasses are calculated under formulas above mentioned and are given in Fig. 2. The maximum change in refractive index is observed for glass PG12 ($\Delta n = 0.35$). The refractive index

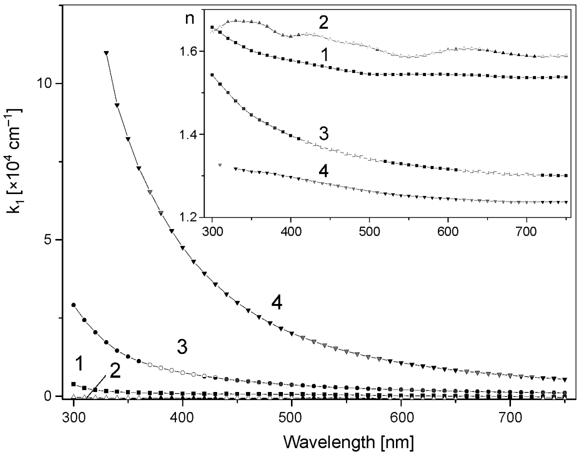

Fig. 2. Absorption spectrum and dispersion refraction for two-phase (curve 1 – 8B, curve 2 – NK) and porous (curve 3 – PG2, curve 4 – PG12) glasses.

curve for glass NK has several local extrema that do not take place for the porous glasses. Thus, the manufacture of porous glasses is accompanied by significant transformation of the absorption coefficient and refractive index spectra.

For the scattering samples with low absorption, one can apply the Gurevich–Kubelka–Munk (GKM) formulae and, upon measuring the diffuse reflection coefficients, find the relationship between the absorption and scattering constants. In the case of a thick layer and diffuse illumination, the following relationship holds [15]:

$$f = \frac{(1-r_d)^2}{2r_d} = m_{kd}\frac{k}{\sigma} = \frac{\chi}{s}$$

where f is the GKM function, r_d is the coefficient of diffuse reflection, χ and s are the absorption and scattering constants, respectively, for a unit thickness layer, m_{kd} is the coefficient, k is the absorption index, σ is the scattering index.

The extinction index is connected with the absorption and scattering indices by the equation $\varepsilon = k + \sigma$. By measuring f, one can define k or σ accurate to a constant factor. If the ratio m_{kd}/σ does not depend on the wavelength, then knowing the function f, one can reproduce the spectrum $k(\lambda)$ quite accurately.

Figure 3 presents the GKM function spectrum for the glasses PG2, PG12, DV1SH, DV1SH-2 and DV1SH-3. The spectra show that the absorption/scattering ratio constants for the two-phase glass DV1SH are higher than those for the porous glasses DV1SH-2 and DV1SH-3, and in the UV region there are the local maxima. Glass PG2 has a local maximum at about 340 nm, and its absorption/scattering ratio constants are higher than those for the glass PG12. The absorption coefficient for the glasses PG2

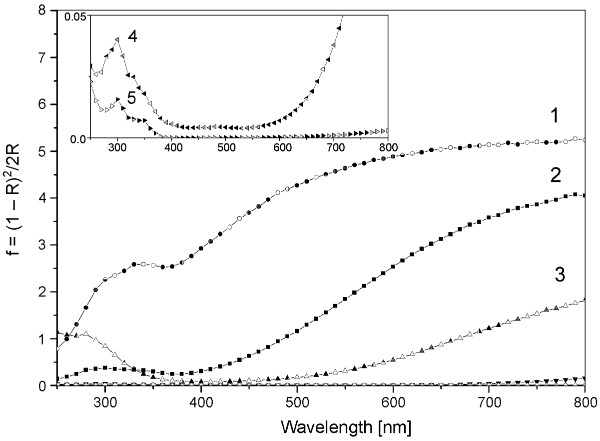

Fig. 3. Gurevich–Kubelka–Munk function for the glasses PG2 (curve 1), PG12 (curve 2), DV1SH (curve 3), DV1SH-2 (curve 4) and DV1SH-3 (curve 5).

and 12 can be determined from transmission spectra, and then one can determine the scattering index from the obtained relationship at 500 nm, for example, $\sigma_{\mathrm{PG2}} = 8.05\times10^{-6}$, $\sigma_{\mathrm{PG12}} = 1.7\times10^{-4}$.

To obtain adequate estimates for the sizes of scattering and absorbing structures, one should properly and correctly select a medium model. The porosity is most commonly evaluated from the Bruggerman equation, but in this case, in addition to measurement of the effective refractive index, it is necessary to know refractive indices for the material of the medium and inside the pores.

For a disperse medium with arbitrary packing density and scattering particles dimensions, the porosity and pore volume can be estimated from the formula for the effective refractive index [16]

$$n_{\mathrm{eff}} = n\left[1 - \frac{NV}{2}\left(\frac{n^2-1}{n^2}\right) - i\,\frac{2N(\pi V)^2(n^2-1)^2}{3\lambda^3 n}\right]$$

where n is the refractive index of the original two-phase glass, N is the number of pores per unit volume, V is the average pore volume, λ is the wavelength.

The formula is obtained for spherical scattering particles of the foreign material (inside the pores), but is suitable also for cylindrical particles of equivalent volume.

Keeping in mind that $n_{\mathrm{eff}}/n = n_{\mathrm{PG}}/n - i(k\lambda/2\pi)$, where n_{PG} is the refractive index of the porous glass, one can estimate the glass pore volume and porosity. Thus, the estimates for the average pore diameter (within the 450–600 nm range) are 7.8–8.2 nm for PG2 and 11.5–12 nm for PG12. The glass porosity estimates are 0.35–0.40 for glass PG2 and 0.65–0.67 for glass PG12.

The leaching process produces pores of unequal sizes and different shapes. This contributes to the light scattering of the samples and, hence, to the estimates. Therefore, the above values are overestimated due to the assumptions adopted in the calculations.

4. Conclusions

The spectrophotometric techniques combined with effective models allow us to obtain the integral estimates being adequate to the real characteristics. The samples for those studies should meet special requirements: they should be property treated before measurements, have sufficient transparence and parallel-plane surfaces and so on. The porous structures are used in microanalytical instruments and devices such as microfilters [2], micropumps [3], columns [4], *etc.* While having a high sorption capacity, the PG can serve as a sensitive component of a bio- or chemo-sensors that forms the indicator complexes as a result of reaction. Optical properties of the PG make it possible to use spectral methods for detection of the complexes. The approaches and estimates presented in this work can be applied to such devices.

Analysis of the transmission spectra of the samples enables finding the spectral ranges being most suitable for estimation of the optical characteristics, based on an appropriate hypothesis. To calculate the absorption/scattering ratio constants of the highly scattering PG, one can apply the Gurevich–Kubelka–Munk theory.

The spectrophotometric data and the effective medium model were used for estimating the sizes and the number of porous structures for absorbing and scattering samples.

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