INTERPARTICLE INTERFERENCE IN THE SCATTERING OF LIGHT BY SUBMICRON-INHOMOGENEOUS GLASSES

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INTERPARTICLE INTERFERENCE IN THE SCATTERING OF LIGHT BY SUBMICRON-INHOMOGENEOUS GLASSES

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Among a number of hypotheses proposed to explain the anomalous phenomena observed in the scattering of visible light by certain submicron-inhomogeneous glasses (the dependence of the scattering intensity I on the wavelength λ as a power p greater than 4, indicatrices elongated backward ($I_{45^\circ}/I_{135^\circ} < 1$), etc.), two of the following currently deserve the greatest attention.

According to the first of them (^{1}), the anomalous phenomena arise as a result of the interference interaction of light waves scattered by different inhomogeneities (particles) formed in the glass in the process of metastable liquation, with radii R from several tens to several hundreds of angstroms. In this case, for the scattering of visible light by an aggregate of particles whose dimensions are smaller than the wavelength of the radiation used, the methods of X-ray structural analysis of liquids are applicable.

The scattering intensity (under the assumption of monodispersity of the particles) is determined by the expression

$$I(k) = A(1+\cos^2 2\vartheta)\lambda^{-4}(m-1)^2 F(k)\left[1+\int_0^\infty 4\pi r^2 g(r)\frac{\sin kr}{kr}\,dr\right]. \qquad (1)$$

Here A is a constant; ϑ is half the scattering angle; $|k| = 4\pi\sin\vartheta/\lambda$; $m = n_1/n_0$ is the refractive index of the particle relative to the medium; r is the distance from the current point to the initial one; $g(r)$ is the function of the radial distribution of particles; $F(k)$ is the form factor for the scattering of an isolated particle.

It is assumed that the phase shift in the passage of the wave through a particle is small, i.e., the condition

$$4\pi R|m-1|/\lambda' \ll 1, \qquad (2)$$

Fig. 1

Figure 1: Fig. 1

is satisfied, where λ' is the wavelength of light in the glass.

From this point of view, the features of light scattering by an aggregate of particles, as compared with scattering by a single particle, are due to an increase in intensity when the parameter $\sin\vartheta/\lambda$ is increased from $0.5 \cdot 10^{-4}$ to $3 \cdot 10^{-4}$ Å^{-1}, with its tending to a maximum located at still larger values of $\sin\vartheta/\lambda$, inaccessible in experiments using radiation from the visible region of the spectrum. With a decrease in the ratio of the total volume occupied by the scattering particles to the total volume of the body, the anomalous phenomena should gradually change into normal ones, which for isolated spherical particles satisfying condition (2) are described by the Gans–Rayleigh–Rocard formula.

According to the second explanation ($^{2-4}$), the anomalous phenomena are a consequence of the existence in submicron-inhomogeneous glasses of regions analogous to Guinier–Preston zones of the second kind, which, it is assumed, exist in aging metallic alloys. The zones are spherical formations in a matrix with refractive index n_0, consist-

consisting of a central particle–a core of radius r_1 (refractive index $n_1 > n_0$) and the spherical layer surrounding it of radius r_2 (refractive index $n_2(r) < n_0$). Each such individual zone scatters visible light anomalously.

The purpose of the present work was to clarify the actual causes responsible for the anomalies observed for sodium silicate and sodium borosilicate glasses. For the former, the values of the exponent p and turbidity τ were compared with structural data obtained by the method of small-angle X-ray scattering.

Glasses annealed in a gradient furnace and quenched in air were investigated. The values of turbidity (for λ 5400 Å) and of the exponent p (in the range

Fig. 1. **A**–dependence of the turbidity of glasses on temperature; **B**–dependence of the exponent p of the wavelength degree $\left(J_{\text{scattering}} \sim \lambda^{-p}\right)$ on temperature. The glasses were annealed in a gradient furnace for the indicated time and quenched in air: **1**–Na 7, 1 h; **2**–Na 12.5, 0.45 h; **3**–Na 14, 1.3 h; **4**–Na 16, 1 h; **5**–Na 19.7, 1 h; **6**–Na 20, 24 h. The crosses indicate points for which $(\overline{\Delta\rho})^2$ was measured and calculated.

from 4100 to 6000 Å) were calculated from the transmission coefficients (5), measured on a spectrophotometer.

X-ray investigations were carried out on a small-angle setup with a slit collimator and a scintillation counter. From the curves of intensity as a function of scattering angle, the values of the mean squares of the fluctuations of electron density $(\overline{\Delta\rho})^2$ (6) and the radii of the regions of inhomogeneity were calculated, assuming their spherical shape. To obtain absolute values of $(\overline{\Delta\rho})^2$, a standard sample of porous glass was used, for which this quantity, established from independent measurements, proved equal to (0.091 ± 0.007) $(e^-/\text{Å}^3)^2$.

It is seen from Fig. 1 that in the glasses studied there exists a temperature region where the exponent p changes hardly at all and has, for a glass of the given composition, the largest value $p_{\max}$, and that with an increase in the sodium oxide content in the glasses there is a gradual decrease of the largest values of p from anomalous to normal, close to 4 (glass Na 20).

The values $(\overline{\Delta\rho})^2_{\text{exp}}$ and $p_{\max}$ are given in Table 1. It also gives the values $(\overline{\Delta\rho})^2_{\text{calc}} = (\Delta\rho)^2 W_{\text{Si}} W_{\text{Na}}$, calculated with the aid of the "lever rule" applied to the liquidus curve of glasses of the sodium silicate system (7), and data on their densities. In this expression $\Delta\rho$ is the difference of electron densities, and W_{Si} and W_{Na} are the relative volumes occupied

phases enriched, respectively, in silicon and sodium. The results of measurements of $(\Delta\rho)^2_{\text{exp}}$ were reproducible within 8%. The error of the values of this quantity given in Table 1 may reach 20%, which is mainly due to the possible existence of a systematic error associated with inaccuracy in the data on the chemical composition of the standard.

The agreement between the quantities $\overline{(\Delta\rho)^2_{\text{exp}}}$ and $\overline{(\Delta\rho)^2_{\text{calc}}}$ is satisfactory. The exception is glass Na 20. In this case preference should be given to $\overline{(\Delta\rho)^2_{\text{exp}}}$, since the point corresponding to this glass lies very close to the liquation curve, and in the present case a small error in determining the temperature and composition of the glass can lead to a considerable error for $\overline{(\Delta\rho)^2_{\text{calc}}}$.

Table 1

Glass composition	Glass composition	Temperature, °C	Experimental data	Experimental data	Experimental data	Calculated data	Calculated data	Calculated data	Calculated data
Na_2O	SiO_2		$\overline{(\Delta\rho)^2_{\text{exp}}} \cdot 10^5$, in $(e^-/\text{Å}^3)^2$	R, Å	$p_{\max}$	$\Delta\rho \cdot 10^2$, in $e^-/\text{Å}^3$	W_{Si}	W_{Na}	$\overline{(\Delta\rho)^2_{\text{calc}}} \cdot 10^5$, in $(e^-/\text{Å}^3)^2$
7	93	706	37	310	7.5	4.0	0.67	0.33	35
12.5	87.5	666	41	270	7.2	4.3	0.35	0.65	42
14	86	624	49	230	6.4	4.6	0.30	0.70	45
16	84	620	33	220	5.1	4.6	0.18	0.82	32
19	81	578	12	140	4.7	4.8	0.05	0.95	10
20	80	534	13	270	4.0	4.9	0.02	0.98	4

The closeness of the measured and calculated values of $\overline{(\Delta\rho)^2}$ indicates that the values W_{Si} and W_{Na} used in obtaining $(\Delta\rho)^2_{\text{calc}}$ and given in Table 1 are close to those actually existing in the glasses. According to Table 1, when the relative total volume occupied by the particles decreases from 35% to a few percent, the index $p_{\max}$ gradually decreases from 7.5 to 4. This regularity, in accordance with what was set forth above, indicates the decisive role of interparticle interference in the cases under consideration.

Let us note that the decrease in the index p for a glass of a given composition, observed with increasing temperature, is caused by two reasons: first, by the gradual disappearance of interparticle interference and, second, by an increase in the particle radii to values of the order of 600 Å and more. Precisely such changes in structure were found as a result of a detailed electron-microscopic study of glass Na 14 ([7]).

To solve the question of the causes of the anomaly in the case of sodium borosilicate glasses containing 7% Na_2O, 23% B_2O_3, and 70% SiO_2, one can make use of their unique ability to be leached without substantial disruption of the geometry of the silica skeleton. The sizes and shape of the pores formed in the specimen correspond to the geometry of the regions of inhomogeneity occupied in the initial glass by the sodium borate component ([8]). Therefore, if the porous glass is filled with some transparent substance having such a refractive index n_1 (whether greater or less than the refractive index n_0 of the medium, in this case the silica skeleton) that condition (2) is fulfilled, then, from the point of view of the ideas of interparticle interference, the spectral dependence should remain unchanged (anomalous) in comparison with the original unleached glass; only the absolute value of the intensity should change.

From the point of view of the ideas of Guinier-Preston zones, however, the necessary condition for the existence of the λ^{-8} dependence is observance of the compensation condition (2), i.e., fulfillment (under the assumption of recti-angular boundaries of the zone) the equality

$$(n_1^2 - n_2^2)r_1^3 = (n_0^2 - n_2^2)r_2^3. \tag{3}$$

It is obvious that, if one assumes (3) to be satisfied in the original glass, then in a leached specimen whose pores are filled with air, or with a liquid having a refractive index different from that of the sodium-borate regions, condition (3) will not be satisfied. It can readily be shown that violation of (3), with r_1 and r_2 constant, leads to a decrease in p; moreover, if $n_1 \leq n_2$, then $p \leq 4$.

Table 2

Object	Refractive index, m	Phase shift $4\pi R(m-1)/\lambda$, $R = 500$ Å, $\lambda = 5800$ Å	Turbidity τ, cm^{-1}, λ 5000 Å	p
Original glass	–	–	0.6	8
Porous glass filled with water	0.69	0.45	2.0	7
Porous glass filled with water	0.91	0.13	2.2	8
Porous glass filled with toluene	1.027	0.04	0.2	10
Porous glass filled with bromobenzene	1.08	0.13	1.1	9

The results of the corresponding experiment are given in Table 2. As is seen from the table, filling the pores with various liquids or with air leaves p anomalous. We note that the increase of p to 9 and 10 when bromobenzene and toluene are used is explained by the dispersion of m, the refractive index of the inhomogeneity (the filled pore), relative to the silica framework. In the case of the first liquid, the factor $(m-1)^2$ entering (1) is proportional to $\lambda^{-1.5}$, while in the case of toluene it is proportional to λ^{-2}. For water this factor is practically independent of wavelength.

Thus, the experimental results indicate interparticle interference as the cause of the anomalies in sodium borosilicate glass.

Consequently, in all the cases we have investigated, the anomalies of light scattering are a consequence of interparticle interference. The assumption that Guinier-Preston zones of the second kind exist in these cases is not necessary. These zones, apparently, can exist only at earlier stages of glass decomposition, when the relative volumes occupied by the phases that arise are still far from their final equilibrium values. It is apparently just such a case that was observed for some glasses in work (4).

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