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## Letters to the Editor

# Detection of platinum atoms in optical glasses by a light scattering method

STANISŁAW GĘBALA

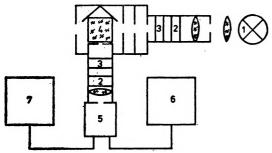
Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

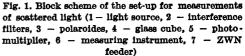
JÓZEF SARZYŃSKI

Optical Works, Jelenia Góra, Poland.

#### 1. Introduction

In order to achieve high quality glasses new melting technologies are applied in which among others platinum or platinum alloy crucibles are employed. Some negative consequences are, however, connected with melting in platinum crucibles due to penetration of some quality of platinum into the glass. This quality is proportional to the erosive and corrosive properties of the liquid glass. Platinum may occur in glass in the ionic  $(Pt^{4+}, Pt^{2+})$  or atomic  $(Pt^{0})$ form. Definite optical properties are connected with each of these forms. The penetration of the ionic platinum results in absorption bands attributed to d-d transitions and located near the border of the visible and ultraviolet light spectra and very weak in the visible range as well as in the luminescence within the 500-800 nm spectral range.





 $Pt^0$  in glass evokes an increased absorption within the whole visible range, which causes the glass to grow grey. This effect follows from the light scattering and depends on the sizes and concentrations of the molecules.  $Pt^0$  is a good nucleator and easily creates heterogeneous dispersive colloidal particles responsible for the scattering of light. Under these circumstances we deal with the colloidal scattering and colloidal change in glass colour.

The examination of platinum ions and platinum atoms in glasses are the preliminary stage [1-4]. The examinations of the effects due to Pt<sup>0</sup> on the absorption in glasses have been carried out in the papers [1].

In this work the measurement results of the light transmission, the scattered light intensity and the coefficient of the polarized scattered light for the glasses melted in ceramics and platinum crucibles are presented. The results have been obtained by using comparative methods. To prepare the glasses to examinations a part of the glass melted in ceramics was next remelted in platinum crucibles and then both parts were annealed commonly.

The measurements of transmission were performed on a Specord UV VIS spectrometer. The scattered light was measured in a setup, the block scheme of which is shown in Fig. 1.

#### 2. Results and discussion

A characteristic feature of the glasses containing Pt<sup>0</sup> is nonselective reduction of their transmission in the visible spectrum range, which gives the glass a gray shade [1]. This results from the light scattering in the atomic platinum colloidal particles of strongly differentiated sizes. In Fig. 2 the transmission in the samples made of F1, SF9 and SF3 glasses melted in platinum is given with respect to the same glasses melted in ceramics. In the glasses examined

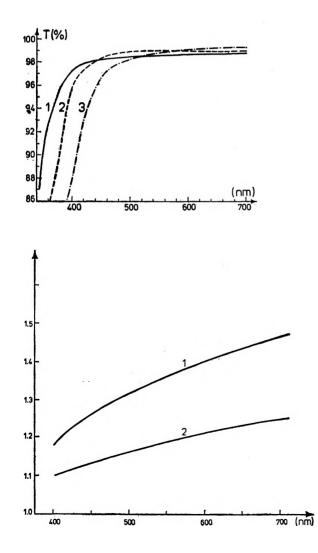
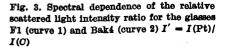


Fig. 2. Spectral dependence of the relativ light transmission for the glasses F1 (curv 1:F1(Pt)/F1(C)), SF9 (curve 2: SF9(Pt) /SF9(C)), SF3 (curve 3:SF3(Pt)/Sf3(C)



the magnitude of absorption bands at the UV and visible range border suggests that the most part of platinum appears in the ionized form. Nevertheless, a nonselective reduction of transmittivity may be noticed in the visual range which is connected with the presence of the atomic platinum.

Glass	e <sub>h</sub>		4h		4 <del>0</del>		<b>⊿</b> ₀	
	Pt	C	Pt	C	Pt	Ø	Pt	σ
Bak4	0.30	0.36	3.33	2.77	0.111	0.095	0.43	0.83
PSK3	0.69	0.74	1.45	1.35	0.044	0.041	0.103	0.092
F1	0.46	0.66	2.17	1.51	0.096	0.086	0.27	0.19
S <b>F1</b> 05	0.65	0.73	1.53	1.36	0.071	0.061	0.17	0.136
sf9	0.52	0.64	1.92	1.56	0.072	0.052	0.20	0.13

Parameters of the polarized light scattered in glasses ( $\lambda = 580$  nm)

A comparison of the scattered light intensity in F1 and Bak4 glasses melted in ceramics and platinum is shown in Fig. 3. The spectral dependence of the intensity ratio (I' = I(Pt)/I(O))upon the wavelength is shown for the scattered light measured under the angle 90<sup>0</sup>. The light wavelength was selected by the interference filters at the input and output of the glass cube.

The growth of the intensity ratio with the light wavelength may be explained by an increase of microheterogeneity in glasses melted in platinum.

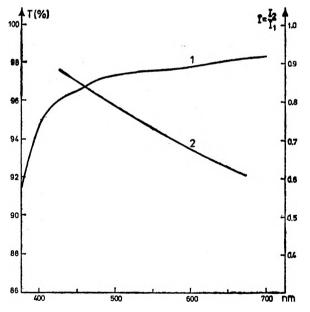


Fig. 4. Spectral dependence of the relative transmission (curve 1:  $F^2(Q, i)/F^2$ ) and the relative scattered light intensity (curve 2:  $I_2F^2(Q, i)/I_1(F^2)$ ), for the glass  $F^2$  after thermal processing (720 K, i = 1 h)

The measurement results for the scattered polarized light presented in Table are given in the form of standard coefficients for  $\lambda = 580$  nm. The Krishnan parameter  $\varrho_h = I(VH)/I(HH)$  connects the values  $\varrho_h < 1$  with the presence of heterogeneity in the glass [5]. The value of  $\varrho_h$ , for the glass melted in platinum is always less than that for the glass melted in ceramics. This indicates an increment of the microheterogeneity. A similar role is played by the reciprocity of the Krishnan coefficients – the depolarizing coefficient  $\Delta_h = I(HV)/I(VH)$  – while the coefficient  $\Delta_v = I(HV)/I(VV)$  is an indicator of anisotropy in microheterogeneity in the glass. This coefficient is of greater value in the glass melted in platinum than in the glasses melted in ceramics. The coefficients  $\Delta_0$  connected with the sizes of microheterogeneity has been calculated earlier from the formula  $\Delta_0 = 1 + \Delta_h/1 + (\Delta_v)^{-1}$ .

The measurements of the scattered light allows to distinguish the glass melted in ceramics from that melted in platinum. Such measurements may give also some information about the states of polyvalent ions in glasses and about the dependences of the properties of these ions upon the thermal processing, among others. For example, the sample of F2 glass melted in platinum was subject to the thermal postprocessing at the temperature 720 K during 1 h. The results are presented in Fig. 4. The curve 1 shows the spectral dependence of sample transmission after the thermal processing with respect to that of the sample not subject to this process.

The results obtained indicate that two types of reduction processes, i.e.,  $Pt^{4+} \rightarrow Pt^{2+}$ (the increase of the absorption band at the border of the UV and visible spectrum [4]), and also of  $Pt^{2+} \rightarrow Pt^0$  (nonselective reduction of transmission) take place. The spectral dependence of the scattered light intensity ratio in glasses after and before the thermal processing (curve 2) indicates an increase of microphase sizes. These results show the possibility of observation of changes in polyvalent ions states in the glass depending upon various physical factors.

#### References

- [1] RINDONE G.E., RHOADES J.L., J. Am. Ceram. Soc. 39 (1956), 173-180.
- [2] GINTHER R.J., KIRK R.D., J. Non-Crystal. Sol. 6(1971), 89-100.
- [3] GINTHER R.J., KIRK R.D., [in] Tenth International Congress on Glass, Japan, Kyoto 1974, No. 6, pp. 1-8.
- [4] STROUD J.S., J. Am. Ceram. Soc. 54 (1971), 401-406.
- [5] SCHROEDER J., Treatise on Materials Science and Technology, Ed. Minoru Tomozawa, Vol. 12, Academic Press, New York 1977, pp. 158.

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### A generalized speckle interferometry method for measuring the arbitrarily oriented (small) displacements of a rigid body

WACLAW URBAŃCZYK, IRENEUSZ WILK

Institute of Physics, Technical University of Wroclaw, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

#### 1. Introduction

In the paper [1] a simple speckle interferometry method has been presented for measuring the rigid body displacements oriented perpendicularly to both the free propagating laser beam illuminating the object and the reflected beam producing the respective speckling pattern. Also, the lower and upper bound limits of the measuring range were there discussed.