

Luminescence due to platinum complexes in optical glasses

Part I. Lead-silicon glasses – preliminary examinations

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In this paper, being part I of a series of three papers, preliminary results are presented of Pt luminescence examinations in optical glasses belonging to flint (F) and heavy flint (SF) groups. The comparative examinations were carried out using the glass melted in a ceramic crucible as a reference sample, the sample examined being made of the same glass but melted in a platinum crucible. The differences in the luminescence spectra of the examined materials were explained by the presence of the platinum ion complexes. The latter resulted from the corrosive and erosive actions of the fluid glass mass on the crucible surface. Besides, the luminescence spectra of platinum were presented for different glass compounds and temperatures. Part II will be devoted to systematic studies of the same glasses, while in part III the controlled doping of platinum will be examined in light glasses (crowns).

1. Introduction

In the optical glass production the crucibles made of pure platinum or of platinum-iridium or platinum-rhodium alloys are used more and more frequently. During the melting process some quantity of platinum penetrates the glass due to the corrosive and erosive actions of the fluid glass mass. As far as minimization of the platinum losses is concerned the problem of corrosion and erosion effects was considered in [1, 2]. There exists an extensive literature allowing us to formulate many technological rules and requirements concerning the raw materials to be used. However, the properties of glass contaminated by platinum (due to corrosion and erosion) have not been examined carefully enough. There are also very few data available concerning the properties of platinum ions in glass. These data inform only about the absorption spectra of metals of platinum group [3], in the silicon and silicon-lead glasses, while the problem of platinum luminescence in silicon glasses [4] has been only mentioned.

In the second degree of oxidation platinum may exist as the ion Pt^{2+} of d^8 electron configuration or in the fourth degree of oxidation, as the ion Pt^{4+} of d^6 electron configuration. The Pt^{2+} ion creates the plane-quadratic complexes of D_{4h} symmetry. The dis-

tribution of energy levels for the same complex is the following: ${}^1A_{1g}$, 3E_g , ${}^3A_{2g}$, ${}^3B_{1g}$, 1A_g , 1E_g [9]. The lowest energy transition of d-d type is ${}^1A_{1g} \leftrightarrow E_g$. This is associated with a very weak absorption band in the longwave part of the visible spectrum. The next d-d transition is ${}^1A_{1g} \rightarrow E_g$, whose absorption band for the PtCl_4^{2-} complex exists near 500 nm. The absorption band connected with the third transition still exists within the visible spectrum near 400 nm. The bands existing between 300 and 400 nm correspond to the transitions ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{g1} \rightarrow {}^1E_{2g}$. The longwave wing of the band (${}^1A_{1g} \rightarrow {}^1A_{2g}$) overlaps partly the visible spectral range. The luminescence is connected with the transition ${}^3E_g \rightarrow {}^1A_{1g}$. This is the transition of triplet-singlet and spin-forbidden type. The luminescence band may be found in the red spectral range (~ 700 nm). So far luminescence has been examined most carefully for PtCl_4^{2-} and PtBr_4^{2-} complexes [5–7, 9, 10], while no works devoted to compounds of platinum with oxygen are known to the authors. The Pt^{4+} ions creates the octahedric complexes of O_h symmetry and possesses unfilled levels (Z^2 , $x^2 - y^2$). These offer the following excitation states: ${}^3T_{1g}$, ${}^3T_{2g}$, ${}^1T_{1g}$ and ${}^1T_{2g}$. The absorption is connected with the transitions from the fundamental level ${}^1A_{1g}$ to the levels ${}^3T_{1g}$ and ${}^3T_{2g}$, and so on. The luminescence is due to the transition from the ${}^3T_{1g}$ level to the ${}^1A_{1g}$ level. This is the spin-forbidden level and the luminescence belongs to phosphoroluminescence of the lifetime 10^{-4} s [5, 6]. PtCl_6^{2-} and PtBr_6^{2-} belong to the best examined complexes of the Pt^{4+} ion [5–8, 11]. For these complexes the absorption bands are positioned in the vicinity of the wavelengths 367, 448 and 490 nm and the observed luminescence shows a maximum at 680 nm [5]. However, no works devoted to the compounds of Pt^{4+} ion with oxygen are known so far.

The purpose of this work was to examine the luminescence of platinum in glass.

2. Method of examinations

The samples to be examined were prepared from the current melts of optical glasses produced in Jelenia Góra Optical Works (Poland). From the glass melted in the ceramic crucible the suitable cubes were cut out, while the rest was remelted in a platinum crucible to produce another sample. Next, both the samples were subject to the same process of thermal processing. The measurements were performed for the glass cube polished on all four sides of sizes $13 \times 14 \times 30$ mm. The examinations of optical absorption were carried out by using the Specord UV VIS spectrophotometer in the ultraviolet and visible ranges. The measurements in the infrared region were performed with the help of the Specord 61NIR.

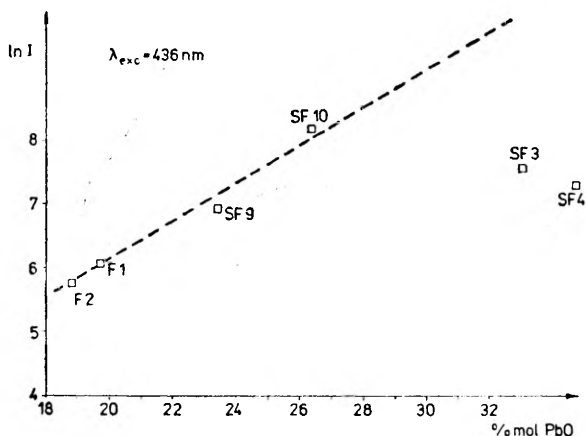
The luminescence spectra were examined on a measuring setup composed of the UM-2 monochromator, the M12FC51 photomultiplier of S20 photocathode and the sensitivity range 320–800 nm, and the G1B1 plotter. The luminescence was excited by the HBO-50 mercury lamp equipped with interference filters for 365 and 436 nm lines. For the same purposes, a halogen lamp with interference filters was also used. The obtained luminescence graphs were normed with respect to the photomultiplier sensitivity. The examinations were carried out at the room and liquid nitrogen temperatures.

The luminescence excitation spectra were recorded in a setup composed of a deuterium (or halogen) lamp, the SPM-2 monochromator with a quartz prism, glass and in-

terference filters, the M12FC51 photomultiplier, and the G1B1 plotter. The optical systems of the above setups were shown in [12].

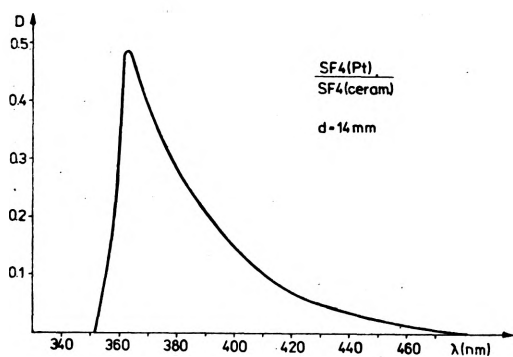
Also, the chemical analysis of the impurity composition in the examined glass was carried out, a special attention being given to metals of platinum group.

3. Results of examinations



In Figure 1 the dependence of the luminescence intensity upon the molar concentration of the lead oxide in the examined glasses is shown. The y axis presents the maximal luminescence intensities which are generated when exciting with a HB-50 lamp via a set of filters of 436 HgMon and 436 JE types.

Fig. 1. Dependence of the luminescence intensity logarithm upon the percentage composition of the lead oxide in glass



As may be seen from this figure the luminescence intensity is by no means a simple function of the PbO content in the glass. The reduction of the luminescence intensity in SF3 and SF4 glasses may result from intensity attenuation due to an increase in the Pt concentration.

Fig. 2. Dependence of the optical density ($d = 14$ mm) in the SF4 glass sample melted in platinum as referred to the similar sample melted in ceramics

In Figure 2 an example of absorption in the examined glass is shown within the interval ranging from the near ultraviolet to 550 nm. The absorption in plates of 14 nm thickness was measured by the difference method by comparing the glass melted in platinum with the same glass melted in ceramics. Optical density is marked on the y axis. The shape of the absorption curve is deformed from the ultraviolet side due to high eigenabsorption of the examined glasses. In all these glasses the absorption spectra were of similar character differing only by the absorption value.

The luminescence spectrum in the SF4 glass is shown in Fig. 3, where the luminescence excitation spectra are also marked. A deuterium lamp was used to excite the luminescence. The excitation spectra were positioned between 300 nm and 500 nm, while the lu-

minescence spectra might be found between 500 and 800 nm. The distribution of luminescence spectra as well as the respective excitation spectra for the sample melted in platinum are marked by the letter *p*, while the result for glass melted in ceramics are marked by the letter *c*. Curve 1 for the excitation spectrum in the band 600–800 nm was obtained

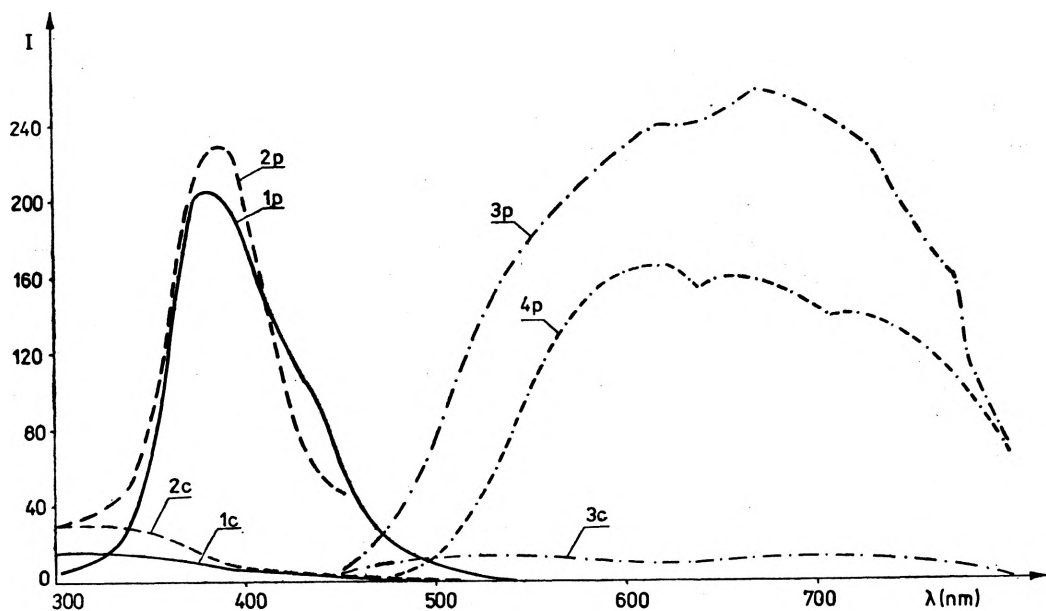


Fig. 3. Excitation spectra and spectral distributions of luminescence in the samples of SF4 glass melted in ceramics (*c*) and remelted in platinum (*p*). Luminescence intensity in relative units. Measured excitation spectra: 1*c* – through the RG2 filter 600–800 nm, 1*p* – through the RG2 filter (600–800 nm), 2*c* – through the VG9 filter (500–600 nm), 2*p* – through the VG2 filter (500–600 nm). Spectral distribution of luminescence: 3*c* – $\lambda_{\text{exc}} = 365$ nm, 3*p* – $\lambda_{\text{exc}} = 365$ nm, 4*p* – $\lambda_{\text{exc}} = 436$ nm

by recording through the RG2 filter, while curve 2 was obtained through the VG9 filter. The existence of another excitation band may be noticed in 500–600 nm band on curve 1 in the longwave region. The basic difference between the samples melted in ceramics and platinum may be observed both in the excitation spectra and in the luminescence spectral distributions. The character of luminescence spectra in all the examined examples of heavy flints is the same. Several luminescence bands positioned side by side may be distinguished in the curves obtained.

Figure 4 shows the luminescence spectra for SF10 glass for the excitation by 365 and 436 nm lines at the room (a) and liquid nitrogen (b) temperatures. The lowering of measurement temperature results in an increase of the longwave luminescence band intensity (650–800 nm).

The chemical analysis of impurities based on the atomic absorption method and made on the Perkin-Elmer model 403 apparatus by using the graphit cuvette of HGA-70 type showed some traces of platinum in the glass melted in platinum. For instance, for the SF10 glass the existence of $2.07 \cdot 10^{-4}$ percentage by weight of platinum was stated. Its degree of oxidation was not determined.

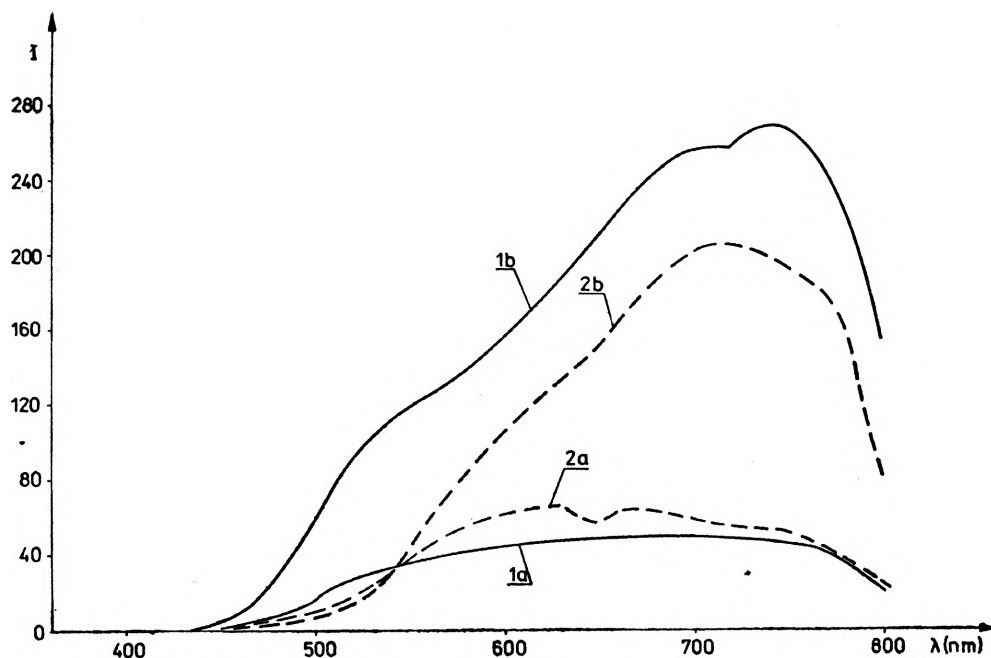


Fig. 4. Spectral distribution of luminescence in the SF10 glass sample measured at the room and liquid nitrogen temperatures. Luminescence intensity in the relative units. Spectral distribution of luminescence: 1a - $\lambda_{exc} = 365$ nm, $T = 290$ K; 1b - $\lambda_{exc} = 356$ nm, $T = 77$ K; 2a - $\lambda_{exc} = 436$ nm, $T = 290$ K; 2b - $\lambda_{exc} = 436$ nm, $T = 77$ K

4. Discussion of results

The fact that polyvalent ions cause a more intensive coloration of the lead glass than of the silicon glasses is well known to technologists. This more intensive coloration is due to several factors, which should be here mentioned:

- i) higher states of oxidation of polyvalent ions in the lead glasses,
- ii) higher absorption cross-section for polyvalent ions in these glasses,
- iii) displacement of absorption maxima toward the longwave side of the spectrum, i.e., toward the higher sensitivity of the eye.

In addition to the above factors, the higher density of lead glasses resulting from more dense packing may be also of some significance. The chemical potential of oxygen as well as the strength of oscillators increase in the lead glasses. The greater strength of oscillators in the lead glass is due to the lower symmetry of the ligand field.

The fundamental result following from the performed examinations is the statement of a relatively high luminescence intensity in the lead glasses melted in platinum. This luminescence is excited in the near ultraviolet region as well as in the shortwave part of the visual spectrum. This may restrict the practical applicability of those glasses. Negative influence of the melting processes performed in the platinum crucibles on the properties of some special glasses (for instance, neodymium glass) used for high power lasers is a well known fact. So far, the applicability of standard optical glasses melted in

platinum has not been questioned by anybody. The luminescence effect may be employed to examine the corrosive and erosive actions of glasses of different chemical composition in the platinum crucible surface.

The results obtained do not allow us to draw all the conclusions concerning the oxidation of Pt or symmetry of local surrounding of these ions. The occurrence of all possible oxidation states of platinum, i.e., Pt⁰, Pt²⁺, Pt⁴⁺ in the examined glasses, which appear in the definite equivalent stoichiometric relations following from the chemical composition of glasses, the raw materials used, and the melting temperatures seems to be the most probable.

To facilitate the interpretation we simplify the problem by assuming that in the glasses examined the complexes of ions Pt²⁺ occur predominantly. The luminescence excitation spectrum and the corresponding absorption band positioned at the border of the visible and ultraviolet light are prescribed to the transition $^1A_{1g} \rightarrow ^1A_{2g}$. In the longwave wing of this band a very weak band exists, which will be prescribed to the transition $^1A_{1g} \rightarrow ^3B_{1g}$. This band may be noticed in the luminescence excitation spectrum, while the luminescence would be attributed to the triplet-singlet transition $^3E_g \rightarrow ^1A_{1g}$, the band of which is positioned in the long-wave part of the visible spectrum. Also the luminescence band located in the region 500–600 nm may be attributed to the transition $^3A_{2g} \rightarrow ^1A_{2g}$. A significant broadening of the bands or the appearance of many bands positioned side by side may be explained by the existence of a variety of Pt²⁺ complexes in the lead-silicon glasses.

The experimental material presented in this work is by no means complete. Actually it presents only the first stage of examination. In view of this the presented interpretation is also of preliminary nature.

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Люминесценция комплексов платины в оптических стёклах.**I. Свинцово-силикатные стёкла – предварительные исследования**

В этой работе, являющейся I частью из серии трёх статей, представлены предварительные исследования люминесценции Pt в оптических стёклах из группы флинтгов (F) и тяжёлых флинтгов (SF). Исследования проведены сравнительным методом, используя в качестве образца отнесения стекло, варенное в керамике, в сопоставлении с испытуемым образцом тех же стёкол, варенных в платиновых тиглях. Отличия в люминисцентных спектрах исследуемых материалов выяснены присутствием комплексов ионов платины. Присутствие ионов платины в исследуемых стёклах является результатом коррозионного и эрозионного воздействия жидкой стекломассы на поверхность сосуда. Кроме того, приведены спектральные распределения люминесценции платины при различных составах стекла и при различной температуре. II часть будет посвящена симметрическим исследованиям тех же стёкол. В III части будут исследоваться контролируемые примеси платины в лёгких стёклах (кронах).