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Influence of oxidizing-reducing melting conditions on the properties of photosensitive glasses**

The subject of investigations was the photosensitive lithium–aluminium–silicate glasses of various contents of basic components and activators (Ag, Ce, Sn, Sb) melted under neutral and slightly reducing conditions. The course of precesses leading to obtaining a permenent visible image was examined by measuring the absorption and photoluminescence spectra at various stages of photothermal processing. These processes, proceeding in slightly different way in glasses melted under reducing and neutral conditions, have been explained by taking account of the differences in the oxidation degree of optical sensitizer ions as well as the influence of melting conditions on the microstructure of higher concentration regions of alkali ions in glass.

1. Introduction

Processes occurring in photosensitive glasses resulting in creation of a visible photographic image may be divided (analogically to those occurring in photographic emulsion) into two stages:

1. Creation of a latent image by exposing the glass to UV-radiation.

2. Development of a visible image by thermal treatment of the irradiated glass at an appropriate temperature.

The possibility of producing a photographic image in glass is conditioned by the presence of some additional components, among which the most important are the photosensitive metals (e.g. Au, Ag, Cu). To accelerate and strengthen the effects of irradiation and thermal treatment of photosensitive glasses optical sensitizer (e.g. Ce, Sm, Pr) and thermoreductors (e.g. Sn, Sb, Cr) are usually introduced.

The conditions for photographic image creation in photosensitive glass were examined earlier [1, 2]. Among others the influence of the presence and concentration of both photosensitive metals and sensitizers in the photosensitive glass, and the conditions of its photothermal processing upon the visible image intensity have been investigated.

The aim of this work is to examine the effect of oxidizing-reducing conditions during melting of glass previously irradiated on the processes leading to production of a visible image.

2. Methodics of examination

The subject of investigation was the lithium–aluminium–silicate glass doped by adding small amounts of silver, cerium and tin or antimony. Two groups of glasses differing in the composition of basic oxides have been investigated while the glasses within each group differed in the content of activators. The chemical compositions (expressed in mole percents) of the glasses examined are shown in table.

No. of glass	Composition in mole percent							
	SiO_2	Al_2O_3	Li_2O	K_2O	Ag_2O	CeO_2	SnO_2	Sb_2O_3
1	71.65	3.80	23.00	1.45	–	–	–	–
2	71.65	3.80	23.00	1.45	0.0095	0.0096	0.0036	–
3	71.65	3.80	23.00	1.45	0.0476	0.0096	0.0036	–
4	71.65	3.80	23.00	1.45	0.0476	–	0.0036	–
5	71.65	3.80	23.00	1.45	0.0476	0.0096	–	–
6	71.65	3.80	23.00	1.45	–	0.0096	0.0036	–
7	71.65	3.80	23.00	1.45	–	0.0096	–	–
8	71.65	3.80	23.00	1.45	0.0476	–	–	–
9	71.65	3.80	23.00	1.45	–	–	0.0036	–
10	73.00	3.90	20.70	2.40	0.0024	0.0098	–	0.0038
11	73.00	3.90	20.70	2.40	0.0097	0.0098	–	0.0038
12	73.00	3.90	20.70	2.40	0.0145	0.0098	–	0.0038
13	73.00	3.90	20.70	2.40	0.0097	–	–	–
14	73.00	3.90	20.70	2.40	–	0.0098	–	–
15	73.00	3.90	20.70	2.40	0.0097	0.0098	–	–
16	73.00	3.90	20.70	2.40	–	0.0098	–	0.0038
17	73.00	3.90	20.70	2.40	0.0097	–	–	0.0038

Ions of elements used to activate the glass may occur in different oxidation degree. The degree of ion oxidation in glass depends first of all upon the oxidizing-reducing conditions of glass-melting. The glasses of chemical composition given in table are melted under neutral and slightly reducing conditions*.

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* These glasses were produced at the Institute of Glass and Ceramics in Warsaw, and at the Optical Works in Jelenia Góra, Poland.

The samples of the examined glasses were irradiated by full light of an analytic quartz lamp of L6/58 type from the distance of about 30 cms and next annealed in an electric furnace at different temperatures ranging from tens up to 550°C.

The processes occurring in the examined glasses during the photothermal processing were investigated by analyzing the results of both light absorption and photoluminescence measurements.

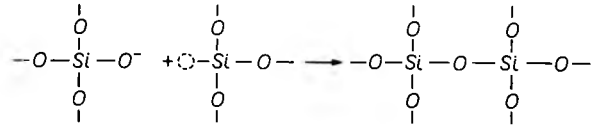
The measurements of absorption were made with the Specord UV VIS spectrophotometer of C. Zeiss (Jena) make. Thin glass plates of 0.1 mm thickness were used for measurement in the case of glasses melted under neutral condition and of 0.5 mm thickness for those melted under reducing conditions.

To carry out the photoluminescence spectrum measurements a typical setup was used in which the luminescence was excited with a high pressure mercury HBO 50 lamp, the light of which being monochromatized with the help of a SPM 2 monochromator equipped with a quartz prism or a UG-glass filter of maximum transmission at 360 nm. The luminescence radiation was directed to the YM 2 monochromator with a glass prism. M 10 FQS 29 photomultiplier was places behind the slit, and its signal was recorded automatically on the tape of the G1 B1 plotter. The read-outs from the plotter were corrected by taking account of the spectral sensitivity of the system composed of YM 2 monochromator and a photomultiplier. The spectral sensitivity of the measuring system limited the measurement range for luminescence to the 400–620 nm wavelength range.

3. Effect of radiation on glass

The photographic image in glass is of spatial type, its depth being conditioned by the UV-irradiation ability to penetrate into the glass. When examining the photosensitive glasses it is essential to determine the limit of fundamental absorption, as the latter characterizes the penetration degree of UV-radiation into the glass.

Short-wave absorption limit for alkali-silicate glasses is connected with the presence of nonbridging oxygen ions in glass and shifts toward the long-wave region with the increasing of both alkali oxide concentration and alkali ion radius [3]. In glasses melted under oxidizing conditions the nonbridging oxygen ion concentration is greater than that in glasses of similar chemical composition but melted under reducing conditions. In glasses melted under reducing conditions a deficiency of oxygen which was removed from the sample during melting, the following bondings can be realized



(1)

which diminish the nonbridging oxygen concentration in glass. Thus in alkali-silicate glasses melted under reducing conditions chemical bonding strength is much greater than in glasses of analogical chemical composition but melted under oxidizing conditions. Hence, in the glasses melted under reducing conditions the energy needed to transfer the electron from a bonding orbital in the complex containing nonbridging oxygen ion to the anti-bonding orbital is also greater. Thus, basic absorption edge shifts toward the short-wave when the conditions of glass melting from oxidizing to reducing ones.

In multi-components glasses (as it is the case for the photosensitive glasses) the spectral position of the basic absorption edge is conditioned by the character of the chemical bonding occurring in glass microregions enriched with alkalies. An introduction of activators into glass changes its transmissivity in UV-region. This is caused by change in bonding strengths, thus in the energy of electron states in glass regions were the activator ions occur as well as by possible optical transmissions in complexes containing those ions.

The transmission spectra of the examined glasses are shown in figs. 1 and 2. The shape of transmission spectrum for glasses doped with cerium but not containing the other activators is striking (fig. 1 —

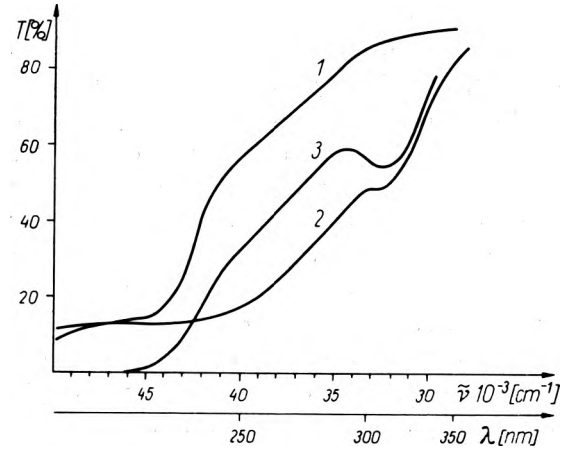


Fig. 1. Transmission as a function of wavelength for glasses melted under reducing conditions not subject to photothermal processing:

1. For glasses containing 0.0097 mole percent of silver but not containing any cerium or antimony, *2*. For glasses containing cerium but not containing silver or antimony, *3*. For glasses containing cerium, antimony and 0.0145 mole percent of silver. The glass plate thickness amounted to 0.5 mm

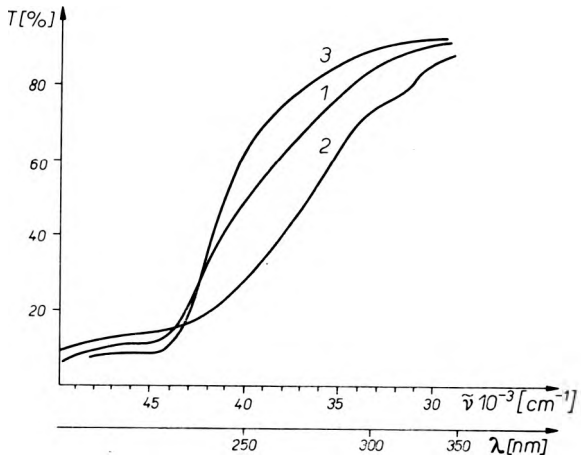


Fig. 2. Transmission as a function of wavelength for glasses melted under neutral conditions not subject to photothermal processing:

1. For glasses containing cerium, tin and 0.0476 mole percent of silver, *2*. For glasses containing cerium but not containing silver or tin, *3*. For glasses containing 0.0476 mole precent of silver but not containing cerium or tin. The glass plate thickness amounted to 0.1 mm

curve *2*, fig. 2 — curve *2*). It is characterized by a broad absorption band within the wavelength band ranging from 230 to 270 nm and by another absorption band at 313 nm. First band is connected with the presence of Ce^{4+} ions in glass, while the other is caused by electron transitions leading to a change in configuration $4f \rightarrow 5d$ for Ce^{3+} ions [4, 5].

The glasses containing cerium and melted under the neutral conditions do not exhibit any absorption at 313 nm (fig. 2). The absorption band at this wavelength, associated with Ce^{3+} ions occurs only in spectra of glasses melted under reducing conditions.

Irradiation by ultraviolet leads to a decrease of absorption within the 313 nm band which is manifested by a minimum appearing at this wavelength in the spectra of additional absorption (caused by irradiation).

The additional of absorption caused by UV-irradiation of glasses are shown in figs. 3 and 4. Fig. 3 shows the spectra of additional absorption, evoked by irradiation of glasses melted under natural condi-

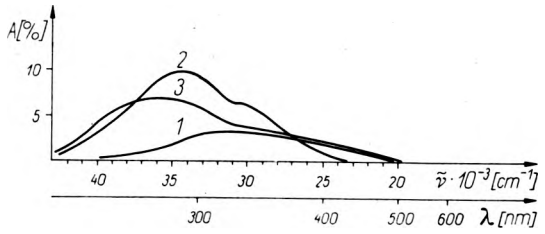


Fig. 3. The increase of absorption as a function of wavelength caused by UV-irradiation for glasses melted under neutral conditions:

1. For glasses containing 0.0476 mole percent of silver but not containing cerium or tin, 2. For glasses containing cerium but not containing silver or tin, 3. For glasses containing cerium, tin and 0.0476 mole percent of silver. The irradiation time — 0.5 h. Glass plate thickness — 0.1 mm

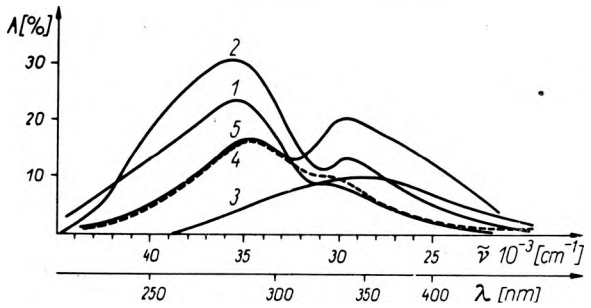


Fig. 4. The increase of absorption as a function of wavelength caused by UV-irradiation for glasses melted under reducing conditions:

1. For glasses containing cerium, antimony and 0.0024 mole percent of silver. *2*. For glasses containing cerium antimony and 0.0145 mole percent of silver, *3*. For glasses containing 0.0097 mole percent of silver but not containing cerium or antimony, *4*. For glasses containing cerium but not containing silver or antimony, *5*. For glasses containing cerium and 0.0097 mole percent but not containing antimony. The irradiation time — 20 min., glass plate thickness — 0.5 mm

tion, while fig. 4 shows the additional absorption spectra of glasses melted under reducing conditions.

From the comparison of the graphs presented in figs. 3 and 4 it may be seen that the spectral position of bands of additional absorption caused by UV-irradiation does not depend upon the percentage composition of basic oxides creating the glass (within the range of compositions under test) being conditioned by the content of activators in glass. The oxidizing-reducing conditions during glass melting do not decide either about the band position in the additional absorption spectrum, but they only influence the band intensity. The UV-irradiated glasses of full content of activators exhibit, independently of both the content of basic oxides melting conditions, an additional absorption of very similar spectrum distribution.

So far the opinions on the nature of the centres responsible for absorption in the ultraviolet range caused by irradiation have not been established. Moreover, the interpretations given by different authors are contradictory [6, 7]. The absorption band centred at 270 nm and creating the latent image in glass was atributed by BEREZHNOY [2] to not quite defined centra containing trapped electrons and connected with the structure of the basic glass. According to the author's experience the most probable defect of glass structure which, after trapping an electron, would cause the absorption of light within this wavelength band is oxygen vacancy.

Intensity of absorption band at about 270 nm caused by irradiation is conditioned by the presence of definite activators in glass. Especially, great absorption increments for band at about 270 nm are observed in glasses melted under reducing conditions and containing cerium and antimony (fig. 4). In the

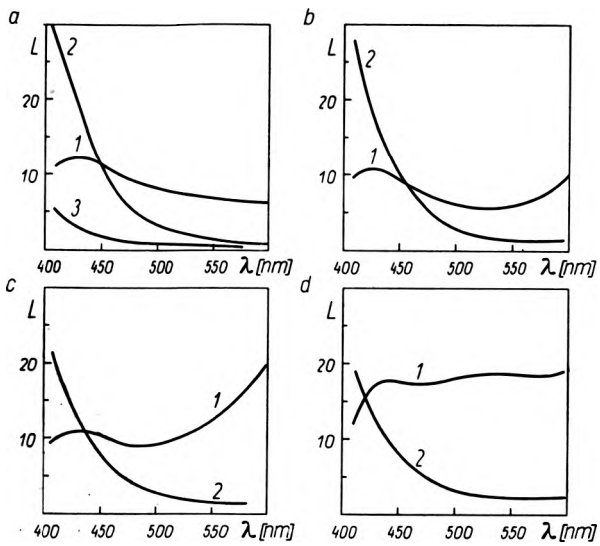


Fig. 5. Luminescence intensity as a function of wavelength, for glasses melted under neutral condition and containing cerium, tin and 0.0476 mole percent of silver:

a) Unprocessed, b) Irradiated by UV-radiation, c) Irradiated by UV-radiation and heated at 265°C d) Irradiated by UV-radiation and heated at 350°C Irradiation time — 45 min. Heating time — 5 min. Luminescence has been excited by monochromatic light: *1.* λ = 365 nm, *2.* λ = 334 nm, *3.* λ = 313 nm wavelength

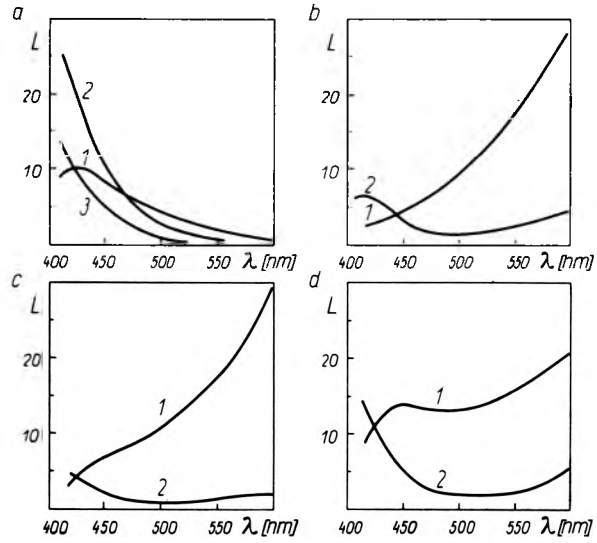


Fig. 6. Luminescence intensity as a function of wavelength, for glasses containing cerium, antimony and 0.0097 mole percent of silver and melted under reducing conditions:

a) Unprocessed, b) Irradiated by UV-radiation and heated at 230°C, c) Irradiated by UV-radiation and heated at 265°C, d) Irradiated by UV-radiation and heated at 360°C. Irradiation time — 30 min. Heating time — 5 min. Luminescence has been excited by monochromatic light of: *1.* λ = 365 nm, *2.* λ = 334 nm, *3.* λ = 313 nm wavelength

glasses melted under reducing conditions the oxygen vacancy concentration should be greater than in glasses of analogical chemical composition but melted under neutral conditions. The creation of additional oxygen vacancies may be caused by antimony ions imbedded in the structure of reduced glasses. The antimony ions require great coordination number and their bonds with the oxygen ions display to a high degree a covalent character. Thus they bind nonbridging oxygen ions preventing formation of bonds described in reaction (1).

A comparison of additional absorption evoked by irradiation of glasses of different activator content, indicates that trivalence ions of cerium are the main source of photoelectrons in glasses. The additional absorption band centred at 270 nm, associated with oxygen vacancies which have trapped the electron, has considerable intensity only in the case of glasses which in their transmission spectra before irradiation contained an absorption band at 313 nm associated with Ce^{3+} ions.

The cerium ions in glass are characterized by intensive luminescence excited by the light of 313 nm and 334 nm wavelengths (figs. 5a, 6a). In glasses melted under neutral conditions the intensity of luminescence excited by the light of 313 nm wavelength is much smaller than in glasses melted under reducing conditions. This is clear if noting that the possibility of luminescence centre excitation is connected with absorption characteristics of glass.

In glass melted under reducing conditions and exposed to UV-irradiation the decrease in both the luminescence intensity of cerium excited by light of 313 nm wavelength and the absorption band at 313 nm, attributed to Ce^{+3} ions, was observed. Thus, the trivalence cerium ions are subject to photoionization due to irradiation. The photoelectrons liberated by this interaction fill the electron traps in the glass structure, among which there are the oxygen vacancies.

The absorption increment within the 270 nm band caused by irradiation of glasses melted under neutral conditions is vanishingly small (fig. 3). In this glasses no decrement in cerium photoluminescence intensity is observed during UV-irradiation of glass.

In glasses free of cerium no considerable absorption increment is observed in the band around 270 nm, independently of melting conditions. In these glasses, in which the photoelectron sources are not Ce^{3+} ions the increment in absorption at 270 nm is small, especially, in glasses melted under reducing conditions.

3. The process of photographic image creation in glasses

The development of latent image is realized by annealing the glass at appropriately high temperature. When the temperature increases up to about 200°C, and the electrons are liberated from the shallow elec-

tron trapps the atomic silver centres are produced in UV-irradiated glass, which are characterized by intensive photoluminescence with the maximum at about 600 nm (figs. 5, 6, 7) and by absorption in both the 320 nm band, and the visual range of spectrum at about 400 nm (fig. 8). In the silver containing glasses, melted under the neutral conditions the produced centres of atomic silver are characterized by a luminescence with maximum at about 600 nm.

Creation of atomic silver in glass is not sufficient condition for development of a permanent visual colouring. Although the atomic silver centres absorb the light in the visual range at about 400 nm, nevertheless the colouring disappears if the temperature increases above 250°C. The changes which begin to occur in the glass melted under the reducing conditions at temperature higher than 250°C depend in a fundamental way upon the presence of antimony. The effect of antimony on the course of processes occurring during thermal treatment at higher temperatures originates from the changes caused by its presence in glass before and after the irradiation. The ions of antimony introduced to glass melted under reducing conditions cause the appearence of additional oxygen vacancies.

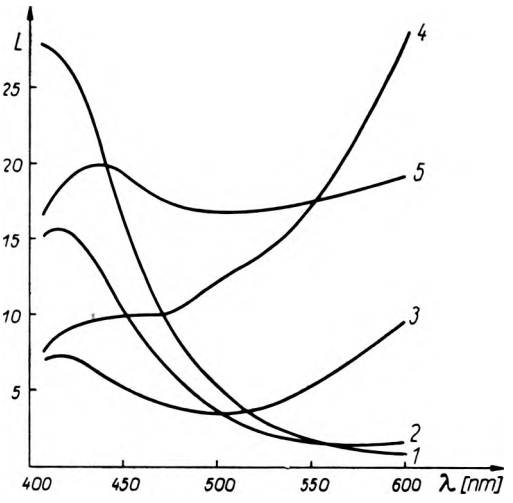


Fig. 7. Luminescence intensity as a function of wavelength, for glasses containing cerium, antimony and 0.0145 mole percent of silver melted under reducing conditions:

1. Unprocessed, *2*. Irradiated by UV-radiation, *3*. Irradiated by UV-radiation and heated at 135°C, *4*. Irradiated by UV-radiation and heated at 250°C, *5*. Irradiated by UV-radiation and heated at 300°C. The irradiation time – 1 h. Heating time – 20 min. Luminescence was excited by the light from HBO-50 mercury lamp with a UG filter

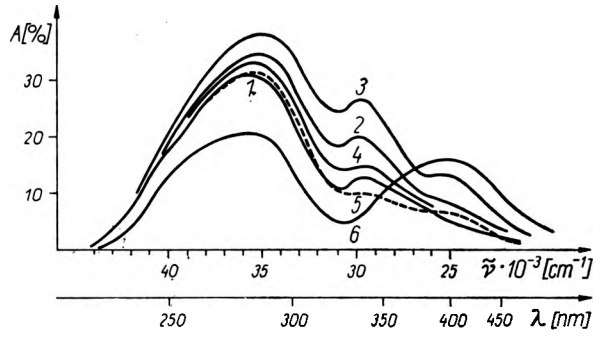


Fig. 8. The increase of absorption as a function of wavelength caused by photothermal processing for glasses containing cerium, antimony and 0.0145 mole percent of silver and melted under reducing conditions:

1. After UV-irradiation, *2*. After irradiation and heating at 130°C, *3*. After irradiation and heating at 200°C, *4*. After irradiation and heating at 300°C, *5*. After irradiation and heating at 320°C, 6. After irradiation and heating at 350°C. The irradiation time – 30 min. Heating time – 10 min. Heating time corresponding to the curve *6* – 20 min. Glass plate thickness – 0.5 mm

While annealing the irradiated glasses of full content of activators at the temperatures higher than 250°C the centres of atomic silver start to suffer from changes, which lower the intensity of absorption band at about 320 nm and 400 nm, and that of the long-wave luminescence band. The luminescence, spectra, however spread to comprise the new band of 500–550 nm wavelength range (figs. 5d, 6d, 7). This new luminescence band should be probably associated with the complex atomic silver centres. Namely, it is more intensive in the case of glasses of high concentration of silver and appeares within this temperature range when the absorption at 320 and 400 nm starts to disappear together with the long-wave luminescence with maximum close to 600 nm, all attributed to centres of atomic silver. Elementary centres of atomic silver are transformed into more complex centres, and exhibit luminescence in the 500–550 nm wavelength range. Thus, this luminescence band indicates creation of atomic silver complex centres, which are nuclei for particles of colloidal silver appearing at slightly higher about 350°C temperatures.

The increase of colloidal silver particles is conditioned by oxygen vacancies filled with electrons present in the glass. The absorption band with maximum at 270 nm which appears as a result of irradiation is attributed to oxygen vacancies. This absorption band connected with oxygen vacancies, that trapped electrons, do not exhibit any changes in intensity under the influence of glass heating up to about 300°C (fig. 8). The absorption increase within this wavelength range, shown in fig. 8, is caused by the increase in absorption band intensity with maximum at 320 nm associated to atomic silver centres.

Due to annealing of UV-irradiated glass of full content of activators at the temperature of about 350°C the intensity of absorption at the 270 nm band diminishes, and a broad absorption band, appears in the visible range of the band close to 400 nm, being commonly attributed to particles of colloidal silver in glass. This absorption band is employed to produce a developed photographic image [1].

The permanent colouration caused by formation

of colloidal silver particles appears after the irradiated glass is annealed in such temperature range, in which the mobility of oxygen vacancies increases. The oxygen vacancies containing the trapped electrons start to migrate within the glass inside carrying the electrons. These electrons can be captured by both the silver atoms and the more complex centres of atomic silver. This ability is indicated by the electron configuration of silver atom $4d^{10}\ 5s^1$ with uncompletely filled subshell $5s$. It is mostly probable that the bondings Ag_2 of particle type with common electrons s will also be created. It cannot be excluded that hybridization of atomic silver orbitals contributes also to this process. If the possibility of creation of Ag_2 boundings between the silver atoms in hybridized state is admitted then for sp type hybridization each atom of silver would have at its disposal two orbitals of sp type containing one electron, while in the case of ds hybridization, in which the orbitals of atomic silver $4d_{z^2}$ and $5s$ could participate each atom would have two orbitals containing three electrons. The Ag_2 particle created by the atoms at the sp hybridization state would contain bonding oribital σ filled with electrons, and unoccupied orbitals capable to create new bonds.

The oxygen vacancies migrating accross the glass play a double role:

1. They provide electrons to populate the free orbitals of atomic silver centres. The negatively charged atoms or silver particles are centres of attraction for the silver ions, thus contributing to the increase of particles.

2. They enlarge the free space, uncocupied by other atoms which is necessary to enable an increase the silver particles as they are located in the immediate neighbourhood of the molcular silver centre.

In the glasses melted under neutral conditions, the number of oxygen vacancies is smaller and they do not play any essential role in the precipitation of colloidal silver in glass. In those glasses the visible colouration appears first at 350°C temperature but rate of absorption increase during prolonged time of annealing of the irradiated glass at this temperature is small. Considerable increases of absorption in the band around 400 nm, especially in glasses of great silver concentrations (denoted in table by numbers 3–5), are observed not either than at temperatures ranging from 400 to 450°C.

4. Conclusions

The photographic process in a photosensitive glass is initiated by photoelectrons liberated due to light absorption. If the glass does not include any optical sensitizers then the radiation quartz must have energy from the basic absorption range to evoke the ionization in glass. The radiation of such energy is intensively absorbed by the glass and for this reason does not penetrate far inside of glass. The optical sensitizers should have a capability of light absorption within a wavelength band which is included in the transmission band of glass. The absorption band due to the presence of sensitizer in glass should be placed within the near ultraviolet range. This requirement is satisfied by trivalence cerium ions, which in the photosensitive glasses under test absorb the light of relatively narrow wavelength range at about 313 nm.

The examined photosensitive glasses melted under reducing conditions have high light transmission in the ultraviolet range and intensive absorption band with the maximum at 313 nm. The radiation quanta absorbed by the ions of optical sensitizer should cause ionization instead of excitation. The rate of changes of cerium luminescence intensity in glass during irradiation by ultraviolet is the measure of photoionization efficiency.

The UV-irradiation of glasses melted under neutral conditions does not cause any diminishing of short-wave luminescence intensity associated with the cerium ions. In the glasses melted under neutral conditions the cerium does not play the role of an optical sensitizer. The source of photoelectrons in those glasses are mainly nonbridging oxygen ions, which contain the most weakly bonded electrons. Nonbridging oxygen ions occur mainly in the microregions of glass enriched in alkalies, where the ions of activators are also located. The glasses melted under neutral conditions exhibit the photosensitive properties at approximately high concentration of silver, depending upon percentage content of alkali oxides in the glass.

Влияние окислительно-восстановительного режима плавки на свойства светочувствительного стекла

Объектом исследований были светочувствительные литиеавоалюмосиликатные стекла с разным содержанием основных компонентов и активаторов (Ag, Ce, Sn, Sb), выплавленные в нейтральном и легко восстановительном режимах. О ходе процессов, приводящих к получению устойчивого видимого изображения, можно было судить на основе спектров поглощения и фотолюминесценции, измеряемых на разных стадиях фототермической обработки. Эти процессы проходят немножко иначе в стеклах, выплавляемых в восстановительном и нейтральном режимах. Они объяснены путем анализа разниц в степени окисления ионов оптического сенсибилизатора и влияния режима плавки на микроструктуру ионогенных областей в стекле.

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