

Spectroscopic studies of the copper-cadmium halide photochromic glasses

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The spectra of optical absorption, luminescence excitation and photoluminescence in the range of 200–750 nm in the Cu-Cd-photochromic glasses were measured. As a matrix of photochromic glass the sodium-borosilicate glass was used. The absorption within the UV wavelength range (200–300 nm) is connected to various structural defects of the matrix glass. The changes of the optical absorption and photoluminescence excitations resulting from the UV radiation in the Cu-Cd-photochromic glasses have been analysed. It was noticed the share of the matrix glass structure components in creation of the colour centers stable of room temperature.

Keywords: copper-cadmium photochromic glass, optical absorption, luminescence excitation, structure defects.

1. Introduction

The photochromic glasses containing copper halides and cadmium halides, as opposed to the well known silver halide photochromic glasses, are characterised by a short darkening time and long bleaching time. The differences as well as the shape invariability of the absorption spectrum induced versus the exposition time and the absence of the optical bleaching the copper-cadmium halide glasses made some researchers suppose that darkening of the glasses is not caused by the creation of colloidal metal particles in the glass, as it happens in the silver-halogen glasses, but is of different character [1–3]. The answer to the question was given by the study [4] wherein, on the basis of the data acquired from the EPR spectra, light absorption and electron microscopy measurements, the colloidal absorption model was elaborated. To the colloidal copper particles dispersed in photosensitive glass phase created by mixed crystals $\text{CdCl}_2:\text{CuCl}$, an absorption band with the maximum at 590 nm was attributed. Since the colloidal metal particles are formed at the peripheries of the photosensitive phase of photochromic glass [5], we have undertaken the investigation of both the photosensitive phase and the matrix glass in the process of creation and destruction of the colour centers. In the spectral investigations, we have concentrated not only on the visible part of the spectrum but we have extended our research work to the spectral

range belonging to the ultraviolet. This was so because in the UV wavelength range, from 200 up to 300 nm, there occur the fundamental absorption edge of the alkali/borosilicate glasses and the absorption caused by additive atoms and structure defects.

2. Experiment

The glass composition used in this investigation was the same as that employed in our earlier works [6, 7]: 62.5% SiO₂, 24.4% B₂O₃, 10.8% Al₂O₃, 12.3% Na₂O (in weight percent). It contained also the halides of sodium, cadmium and copper, which formed the photosensitive phase of the glass.

The samples were irradiated with a mercury arc source through a filter having a peak transmission of 80% at 366 nm and 10% at 310 and 410 nm. The transmittance of the glass samples was measured using a Specord UV–vis spectrophotometer before and after irradiation. The luminescence excitation spectra after the excitation with the light of the wavelengths from the range 200–400 nm were measured with the typical system consisting of a monochromator, photomultiplier tube and recorder.

3. Results and discussion

The absorption spectra of the studied glasses, both photochromic and those not including the photosensitive additives, are presented in Fig. 1. After insertion of the photosensitive additives into the matrix glass, new bands appear in the absorption

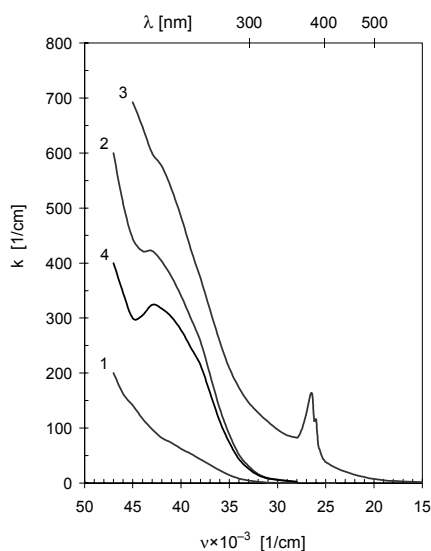


Fig. 1. Absorption spectra of glasses: 1 – basis glass (without photosensitive additives), 2 – with photosensitive additives, before heat treatment, 3 – with photosensitive additives, after annealing at 610°C/1 h (photochromic glass), 4 – the difference between curves 2 and 1.

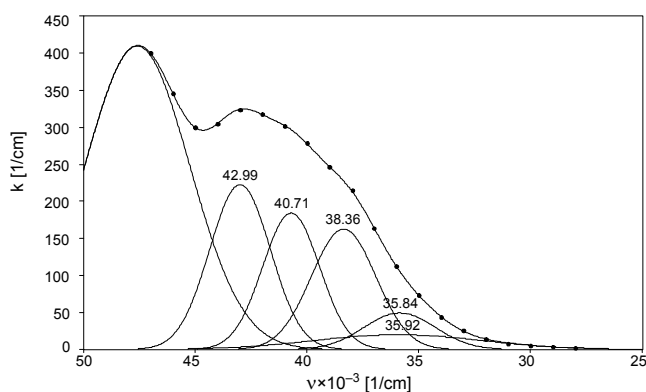


Fig. 2. Deconvoluted spectrum with curve fitting for absorption spectra 4 from Fig. 1. Fitted parameter $r^2 = 0.99998$ (points – experimental data, lines – result of fitting, values – frequencies of the component bands centers).

spectrum (Fig. 1, curve 4). The peak at about 240 nm ($\nu = 41.7 \times 10^3 \text{ cm}^{-1}$) is clearly pronounced while, from the side of the greater wavelengths, there are less intensive absorption bands. These bands became visible after the decomposition into the Gaussian components of the additional absorption caused by the introduction of the photosensitive additives into the glass (Fig. 2).

The glass gains the photochromic properties only after an additional heat treatment at the temperature values T_g or higher. In consequence, there happen the phase separation with isolation of the halide phase having a predefined chemical composition, halide particle dimensions and distribution in glass [8–10]. In the absorption spectrum of such glass (Fig. 1, curve 3), the two peaks appear at 377 and 385 nm ($\nu = 26.5 \times 10^3 \text{ cm}^{-1}$ and $\nu = 26 \times 10^3 \text{ cm}^{-1}$) which are characteristic of the exciton absorption in crystals CuCl [11, 12]. The radiation quant absorption from the exciton absorption band is accompanied by resonance luminescence [11, 13]. The exciton photoluminescence and its excitation spectrum are difficult for measurement due to the strong light scattering of the same wavelength interval. This strong light scattering is caused by microcrystals of the photosensitive phase, created by the process of thermal treating of glass.

The luminescence excitation spectra are presented in Fig. 3. The wide band in this spectrum, falling onto the wavelength range lower than 280 nm ($\nu = 35.7 \times 10^3 \text{ cm}^{-1}$) is characteristic of all silicate glasses. In the case of silica and alkali silicate glasses, the maximum of this band occurs at 240 nm ($\nu = 41.7 \times 10^3 \text{ cm}^{-1}$) while in the case of the more complex chemical composition, the maximum moves towards the greater wavelengths.

A lot of work has been devoted to the investigation of the absorption and emission centers for the radiation in the range of wavelengths 200–280 nm ($\nu = 50 \times 10^3 - 35.7 \times 10^3 \text{ cm}^{-1}$). Most frequently those centers are connected with the germanium, aluminium or iron additive atoms (being the raw material impurities) or with the oxygen

vacancy, or non-bridged oxygen atoms [14, 15]. It may be assumed that the centers connected with the matrix glass structure, that may be modified by the additive atoms, are responsible for this luminescence.

Any glass that has passed the thermal treatment which induce the photochromic properties indicates much stronger intensive luminescence when excited with light of the wavelength of about 260 nm ($\nu = 38.5 \times 10^3 \text{ cm}^{-1}$) than the glass that has

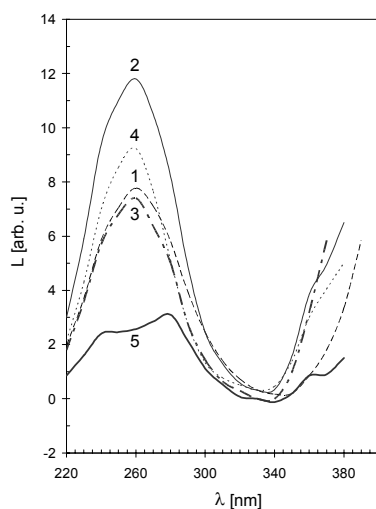


Fig. 3. Photoluminescence excitation spectra of glasses: 1 – with photosensitive additives, before heat treatment, 2 – with photosensitive additives, after annealing at 610°C/1 h (photochromic glass), 3 – photochromic glass after UV illumination, 4 – photochromic glass after many darkening and fading processes, 5 – the difference between curves 2 and 4.

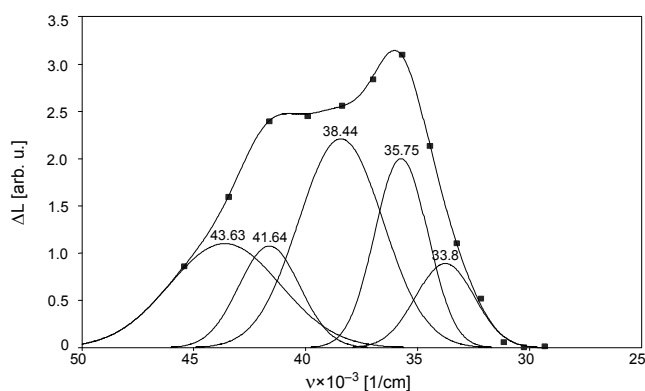


Fig. 4. Deconvoluted spectrum with curve fitting for photoluminescence spectra 5 from Fig. 3. Fitted parameter $r^2 = 0.99945$ (points – experimental data, lines – result of fitting, values – frequencies of the component bands centers).

not undergone such processing (Fig. 3, curves 1 and 2). This is understandable since the absorption centers are responsible for this luminescence. Such centers are connected with the structure defects and they are created during fast quenching of glass. The biggest chances for creation of such defects exist within the extent and on the extremes of the photochromic phase regions.

Illumination of the photochromic glass with the UV light decreases the intensity of luminescence excited with light of the wavelength of about 260 nm ($\nu = 38.5 \times 10^3 \text{ cm}^{-1}$) down to the level that has been observed in the spectrum of the glass containing photosensitive additives but not being subject to the annealing (Fig. 3, curve 3). The electrons and holes released during the UV radiation on the glass fill the traps constituted, among other things, by the thermal defects, thus decreasing the light absorption and emission connected with the defects. The photochromic glass samples being darkened several times by the UV radiation and, next, faded (Fig. 3, curve 4), present a lower value of luminescence excited with light of the wavelengths within the range of 240–280 nm ($\nu = 41.7 \times 10^3$ – $35.7 \times 10^3 \text{ cm}^{-1}$) than the samples not being subject to such process (Fig. 3, curve 2). The analysis of photo-chromic glass photoluminescence changes caused by the UV radiation shows that during bleaching of photochromic glass not all centers responsible for the luminescence excited within the band of 240–280 nm return to the initial state (Fig. 3, curves 2, 4, 5). Some of the centers become inactive after the first illumination of glass. Photoluminescence excitation spectrum of inactive centers is presented in Fig. 3 (curve 5). Deconvolution of this spectrum (Fig. 4) gives the Gaussian components, which energies are in good agreement with those presented in Fig. 2. Thus, these centers that lose the activity are certainly deep traps for the holes and electrons, and are connected both with structure defects and with additive atoms in the glass.

During the course of the photochromic glass darkening process, the main role is played by the thermal structure defects occurring in the photosensitive glass phase. The defects are cationic vacancies in CuCl crystals contained in the photosensitive glass phase characterised by the red photoluminescence, the maximum of which is at about 740 nm [16]. When the UV radiation acts on the photochromic glass, the intensity of the red luminescence decreases fast and the light absorption at the wavelength of about 370 nm ($\nu = 27 \times 10^3 \text{ cm}^{-1}$) (Fig. 5, curve 1 and 2) increases equally fast.

The band within the absorption spectrum at 370 nm ($\nu = 27 \times 10^3 \text{ cm}^{-1}$) was assigned in this study [17] to the ionised molecule of chlorine Cl_2^- which is identified with the cationic vacancy that has trapped the hole. It is because the hole trapped by the cationic vacancy is located at two chlorine ions being the closest neighbours of the vacancy. The above interpretation corresponds to the results obtained in our study. However, the authors of the paper [18], investigating the influence of the UV radiation on the cadmium-borate and cadmium-silicate glasses, assigned the band of the added optical density at 370 nm to Cd^+ ions created due to the illumination of the glass. Such interpretation is not also inconsistent with the results obtained by us since the Cd^{2+} ions being an additive in the CuCl structure are located in the direct neighbourhood of

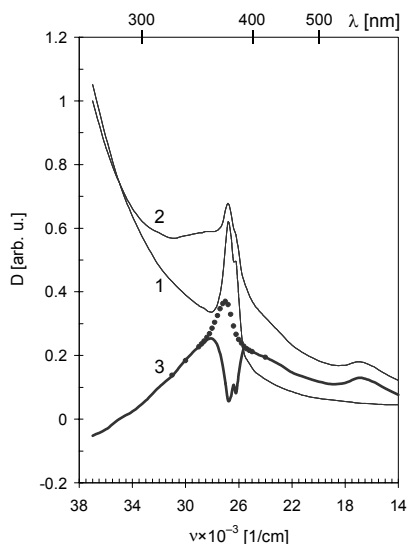


Fig. 5. Optical density spectra of photochromic glass: 1 – before UV illumination, 2 – after UV illumination, 3– the difference between 1 and 2 spectra.

the cationic vacancies. The cationic vacancies are traps for holes, while the Cd^{2+} ions may trap electrons. The interaction of the structure defects with excitons accelerates the CuCl photolysis reaction. An evidence for the occurrence of the photolysis is the decreased exciton absorption represented by a clear minimum at the wavelengths 377 and 385 nm (Fig. 5, curve 3).

As a result of the photochromic glass irradiation, in addition to the band at 370 nm ($\nu = 29 \times 10^3 \text{ cm}^{-1}$), an additional absorption appears within the whole visible spectrum range (Fig. 5, curves 2 and 3). The absorption band with the maximum at 590 nm is assigned to the colloidal copper particles [4]. To create the colloidal particles, electrons, that could neutralize the copper ions, are needed. Their main sources (electrons) are the excitons that disintegrate into holes and electrons. The electrons neutralize the copper ions and the holes locate themselves on chlorine ions situated in the neighbourhood of the cationic vacancies in the CuCl structure.

Our investigations indicate that the disintegration of the centers characterised by the light absorption at 370 and 590 nm ($\nu = 27 \times 10^3$ and $17 \times 10^3 \text{ cm}^{-1}$), that occurs during bleaching of the photochromatic glass, does not occur independently. An evidence for this is the proportional decrease in the added optical density in the two bands. At the same time, the absorption bands at 377 and 385 nm, assigned to the exciton absorption in the CuCl crystals, recover.

When the photochromic glass is bleached at room temperature, the absorption coefficient values for the exciton absorption peaks return to the values before the glass irradiation – the CuCl crystal structure reconstructs. However, this does not mean that

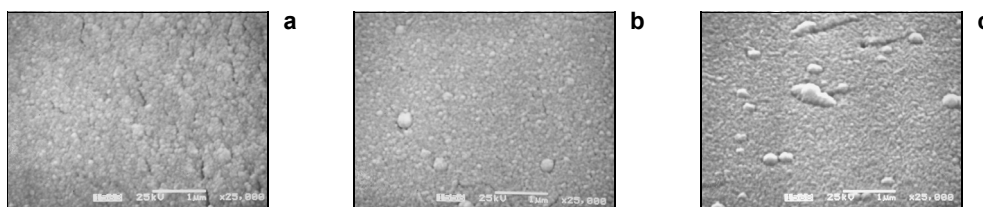


Fig. 6. Electron micrographs of heated glasses: 540°C/1 h (a), 600°C/1 h (b), 630°C/1 h (c).

the photochromic glass darkening process is reversible. There are absorption centers stable at room temperature and they are responsible for the absorption in the range of the wavelengths 240–280 nm ($\nu = 41.7 \times 10^3$ – 35.7×10^3 cm⁻¹). Some percentage of the centers is characterised by absorption at 370 and 590 nm ($\nu = 27 \times 10^3$ and 17×10^3 cm⁻¹).

The colour center percentage, stable at room temperature, is connected with the magnitude and amount of the photosensitive phase areas created within the glass during the thermal treatment. The higher temperature and the longer heating time, the more liquidation drops will precipitate in the glass (Fig. 6) and the bigger percentage of the colour centers stable at room temperature. The stable colour centers undergo destruction at temperatures higher than 100°C. Then, both in the visible and short wavelength spectrum part, the changes caused by the glass illumination retract. This means that the colour centers stable at room temperature, characterised by the visible light absorption, are connected with the components of the structure of the matrix glass that absorbs light from the range of wavelength 240–280 nm.

4. Conclusions

The spectral and luminescent investigations of the copper-cadmium halide photochromic indicate the share of the matrix glass in the process of glass darkening and bleaching. For the spectrum range from 200 up to 300 nm, there falls the absorption attributed to various structural defects of the sodium-boron-silicate glasses, such as oxygen vacancies, broken bonds, non-bridged oxygen atoms binding the additive atoms. Without any doubt, such effects occur at the interfaces between the photosensitive phase and the matrix glass. With the UV radiation, the first glass exposition liquidates some of the effects, what is confirmed by permanently decreased absorption within the wavelength range specified above, observed after the first irradiation of glass.

With the matrix glass structure, there are connected also the colour centers absorbing light from the visible spectrum range, that are durable at room temperature. This result confirms the earlier suggestions that the photosensitive components that are the copper and cadmium chlorides in the glass investigated in the study, are pressed into the surface layer of the liquidation drop during glass cooling after the secondary

thermal treatment. The colour centers produced during glass illumination are created, therefore, in the external regions of the photosensitive area regions. The colour centers neighbouring directly with the matrix glass do not disintegrate at room temperature but at a higher temperature value. The disintegration of the colour centers stable at room temperature happens simultaneously with the reconstruction of the centers connected with the matrix glass structure, characterised by the light absorption within the wavelength interval from 240 up to 280 nm.

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