

Studies of the properties of copper-cadmium photochromic glasses

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The properties of photochromic glasses containing copper and cadmium chloride were investigated. The influence of the temperature and time of heat treatment on the change of the glass structure was considered. The parameters (coefficients) determining the bleaching process were calculated. To study the structure of photochromic glasses after heating the thermally stimulated depolarization technique was applied. The origin of TSDC peaks was discussed.

1. Introduction

Among the various materials exhibiting photochromism, including crystals, liquids and glasses, the inorganic photochromic glasses are attractive from the standpoint of the mechanical and chemical properties as well as freedom from fatigue during the repeated cycling. Photochromic glasses can be homogeneous or contain a separated phase of microcrystallinities with which the photochromic property is associated. Silver-halide photochromic glasses have found application mainly as a material for ophthalmic lenses [1]–[4]. Recently, the photochromic glass containing copper and cadmium chlorides are a subject of investigations [5]–[8]. In contrast to the silver-halide photochromic glasses, which darken by formation of colloidal particles of metallic silver, copper-cadmium halide glasses display very short incubation time for darkening and long bleaching period. For explanation of this behaviour a noncolloidal darkening mechanism is suggested. The darkening results from formation of colloidal copper particles of Cu^+ in CuCl and $\text{CdCl}_2:\text{CuCl}$. These glasses can be applied for recording and storing information. The most important characteristics of photochromic glass are the rates of formation and relaxation of colour centres, the spectral region and optical density of the induced absorption, as well as spectral region and temperature range of activation of a photochromic process.

The aim of this paper was to investigate the properties of the photochromic glasses containing copper and cadmium halides.

2. Experimental

The subject of investigation was the photochromic glass of chemical composition (% by weight): 52.5% SiO₂, 24.4% B₂O₃, 10.8% Al₂O₃, 12.3% Na₂O containing also halides of sodium, cadmium and copper. The glass was heated for different times and at different temperatures. The glass samples differently treated are labelled with numbers 1 to 7 (Tab. 1).

Table 1. The temperatures and times of heating for glass sample.

Glass	1	2	3	4	5	6	7
Temperature of heating [°C]	600	600	600	540	610	630	650
Time of heating [h]	0.25	1	2	1	1	1	1

Measurements of the optical density were carried out with the Specord UV-vis spectrometer, adapted for transmittance measurements during exposition of the sample. The light beam inducing the photochromic darkening of the glass and measuring light beam were perpendicular to each other. The time retardation between the measurements and the end of exposure for all presented results of the measurement amounted to 5 s. As the light source for irradiation a mercury lamp of the wavelength of 365 nm was used. The time of illumination was 5 min.

The structure of photochromic glasses was investigated using the electrical method. The thermally stimulated depolarization current (TSDC) technique was applied. For the thermally stimulated depolarization measurements the sample was polarized by an electric field F_p at a temperature T_p for a time t_p . Then the electric field was switched off. During heating at a constant rate the depolarization current TSDC was registered. The activation energy of the TSDC peaks was determined with a partial discharge technique [9]. The TSDC measurements were carried out by means of computerized automatic system. Before measurements the glass samples were preheated to 450 K to remove the surface moisture. The measurements were performed in the temperature range 100–450 K at a constant rate 5 K/min. The glass samples were of the following dimensions: 20 × 15 × 0.5 mm³ (for optical measurements) and 10 × 10 × 0.5 mm³ (for TSDC measurements).

3. Results

The basic characteristic of photochromic glass is the rate of forming and decay of the light absorption centres. They are formed as a result of irradiation of the glass with electromagnetic waves from the visible and ultraviolet range. Figure 1 presents additional optical density, defined as a difference of the sample optical densities after and before illumination, for glass heated at 600 °C for different time (glasses 1–3) and for glass heated at 650 °C for 1 h (glass 7). An increase in the optical density of glasses heated at higher temperatures and for longer times was observed.

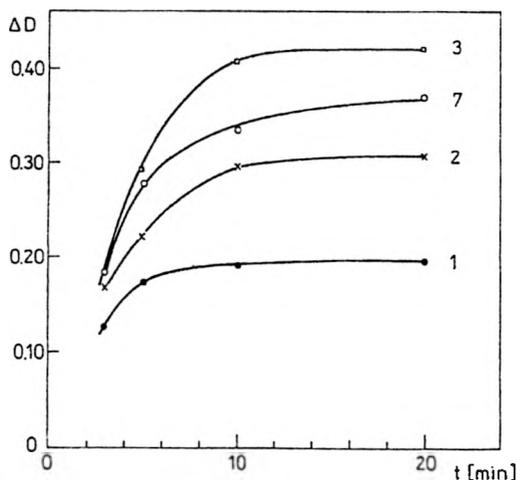


Fig. 1. Dependence of the additional optical density on time of bleaching after irradiation of glass.

More information about decay of the colour centres can be obtained from analysis of relaxation curves. It is possible to distinguish three exponential components of the bleaching process with different time constants. In Table 2, percentage values of the long-time σ_l and slow-time σ_s colour centres are presented. A decrease in the slow-time colour centres and an increase in the long-time centres for glasses after heating at higher temperatures and for longer times can be observed.

Table 2. The values of σ_s , σ_l , $\gamma_{1/2}$, β_l and β_s for the glasses under investigation.

Glass	1	2	3	5	6	7
σ_s [%]	36	23	8	22	17	9
σ_l [%]	47	61	75	62	66	73
$\gamma_{1/2}$ [min.]	26	48	95	48	52	120
β_l [s^{-1}] $\times 10^{-5}$	11.7	7.4	6.0	7.2	6.2	4.8
β_s [s^{-1}] $\times 10^{-3}$	4.2	10.5	13.3	9.9	9.4	8.8

Additionally, the relaxation coefficient γ was determined. It is defined as: $\gamma_\tau = (D_k - D_s)/\Delta D_{\max}$, where τ is the time after the end of the irradiation, D_k and ΔD_{\max} denote the optical density and additional optical density, measured right after the irradiation was terminated. The relaxation coefficient γ_τ can be expressed in percentage and it defines the percentage of the colour centres which decay in the time τ . As a measure of the bleaching rate also the time $\gamma_{1/2}$ can be treated. It is a time after which the additional optical density decreases to half its maximal value measured just after illumination of the sample. The values of $\gamma_{1/2}$ for the glasses under investigation are shown in Tab. 2.

Assuming the time dependence of $\Delta D = \Delta D_{\max} e^{-\beta t}$, it is possible to determine the decay constant β . The obtained values of β_l (for long-time component) and β_s (for

slow-time component) for the glasses investigated are also presented in Tab. 2. From the data collected it follows that the decay constant for the long-time colour centres produced as a result of illumination of the glass decreases but coefficient $\gamma_{1/2}$ increases when the glasses are heated at a higher temperature for a longer time. Moreover, with an increase in the heating time at a constant temperature, the decay constant of the short living centres increases. However, with an increase in the heating temperature, the value of β_s decreases.

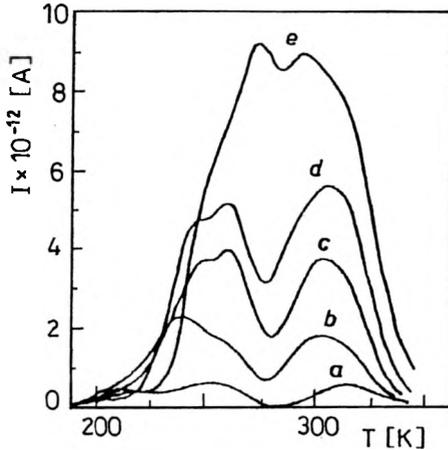


Fig. 2. The TSDC curves for glass 3: $t_p = 10$ min, $F_p = 5 \cdot 10^5$ V/m, $T_p = 253$ K (curve a), 273 K (curve b), 293 K (curve c), 313 K (curve d), 333 K (curve e) and 373 K (curve f).

In Figure 2, TSDC curves for the glass 3 polarized at different temperature are presented. Three TSDC peaks were observed to exist in all the glasses under investigation (besides the glass 4). The magnitudes of TSDC peaks are different for different glasses. Our earlier measurements have shown that two TSDC peaks appear in the initial glass without the photochromic additives. The temperature maximum and the values of activation energy of TSDC peaks of the glasses investigated are similar (Tab. 3, $\Delta E_a = \pm 2$ kJ/mol).

Table 3. Temperature of maximum and values of the activation energy of the TSDC peaks.

Glass	Peak 1 T_m [K], E_a [kJ/mol]	Peak 2 T_m [K], E_a [kJ/mol]	Peak 3 T_m [K], E_a [kJ/mol]
4	260	310	—
	28	34	—
2	250	275	325
	31	42	48
3	245	265	325
	30	42	47

4. Discussion

Before heat treatment the glasses investigated exhibit no photochromic properties. Photochromism develops during the heat treatment. The samples heated at a temperature higher than 600 °C show a distinct opalescence and in the temperature range 600–650 °C are becoming opaque.

The results of our investigation indicate that reaction of glass to light depends on the heat treatment. The higher the temperature and the longer the heating time, the longer living centres are produced inside the glass sample and the decay constant decreases. Therefore, it is clear that the parameter $\gamma_{1/2}$ increases so rapidly. An increase in the half-time of decay can also be explained by the fact that decay constant of the short living centres decreases with an increase in the heating temperature of the glass, the number of these centres being decreased as well. A decrease in the constant β_s , with an increase in the heating time can be explained by expansion of the colour centre areas which are precipitated during the heat treatment. These results are of vital importance from the standpoint of application of the glass containing copper and cadmium as an information carrier.

The TSDC measurements can be useful for investigation of change of the glass structure after heating. The values of activation energy of the d.c. conductivity of the glasses under investigation are higher than the ones obtained from the TSDC peaks. The d.c. conductivity is related with unlimited motion of ions. The TSDC peaks are connected with another type of motion of the sodium ions. In the glasses investigated the sodium ions may be divided between aluminate and borate structural units [10], [11].

The initial glass is homogeneous. After the heat treatment the phase separation into silica, sodium-rich phases and droplets of photochromic phase occurs. Different magnitudes of TSDC peaks in different glasses indicate a change of structure (size of microphases) after heating. The values of temperature maxima and activation energy of the TSDC peaks are similar. This suggests that the origin of TSDC peaks is also similar. The first TSDC peak P1 can be attributed to orientation of sodium ions around $[\text{AlO}_4]^-$ and/or $[\text{BO}_4]^-$ groups. The existence of peak P2 can be related to translation motion of sodium ions (Day's model [9]). These peaks are also observed in glass 4 (without photochromic additives) in which after heating the phase separation appears but it does not exhibit photochromic properties. The origin of P1 and P2 peaks can be supposed to be the same in all the glasses under investigation. The peak P3 does not appear in glass 4. Unlike other glasses, glass 4 does not get dark after illumination of the sample. Therefore, the appearance of peak P3 can be related to the existence of the particles of the photosensitive phase.

The EM-graphs confirm this interpretation. With increasing temperature and time of heating the number of photochromic droplets increases. We also observed changes in the volume of silica and sodium rich phases.

5. Conclusions

The results presented indicate that with an increase in temperature and time of heating of the photochromic glasses containing copper and cadmium, an increase in colour centres and half-time of decay of photochromic colouring is observed.

The measurements of the thermally stimulated depolarization currents show the change of the structure of glasses after heating at different temperatures and times. The appearance of the P1 and P2 TSDC peaks is related to the different ways of motion of sodium ions in glass. The existence of the third TSDC peak is connected with the particles of photochromic phase which is produced after heating at a temperature higher than 540 °C.

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