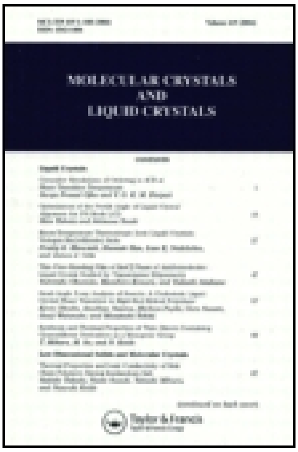

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TAILORING OF PHOTOCHROMIC GLASSES

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Abstract Some ways to control and to improve the properties of silverfree photochromic glasses, including darkening level, fading rate and color, are discussed.

INTRODUCTION

Darkening and fading of a photochromic glass is the result of complex physical and chemical interactions. This is the reason why it is difficult to control the photochromic properties. In this paper we will discuss some possibilities to improve the properties of silverfree photochromic glasses. It centres on the increase of the darkening and of fading rate simultaneously. In addition, a survey will be given on some other possibilities to tailor silverfree photochromic glasses.

PHOTOCHROMIC GLASSES - A SURVEY

The photochromic glasses considered here are composed materials of light sensitive microcrystals, usual silver or cuprous halides, embedded in a glass matrix. The microcrystals are the origin of the photosensitivity. Likewise, the glass matrix is relevant to the photochromism, because it is inert with respect to any product of the 'photochromic' reaction. In addition, the glass matrix is a solvent with variable solubility relating to the components of the photosensitive microcrystals. A suitable matrix glass stabilizes the halide and heavy metal ions of activating components at high temperatures and causes the formation of heavy metal halides at lower temperatures[1].

Preparation of photochromic glasses includes first the fusion of glass. After cooling of the glass melt the added activating ions are still distributed homogeneously in the glass matrix. Second, a heat treatment above Tg is necessary to precipitate the microcrystals. During heat treatment nuclei are formed and then the crystals grow. In addition, it is possible to adjust photochromic properties by a second heat treatment below Tg. The size of the microcrystals is usual from 5 to 50 nm.

Irradiation with UV results in the excitation of the photosensitive microcrystals and produces electrons and 'holes'. It is necessary to catch the 'holes' by trapping, otherwise they would recombine with the electrons. At particular sites on the surface of the crystallites the free electrons react with silver or copper ions and form metal atoms which finally form metal colloids on the surface of the microcrystal. The absorption of the colloids is the origin of the darkening[2].

The trapped 'holes' migrate through the crystal. If they approach the metal colloids then an interaction becomes possible: the metal atoms dissociate into metal ions and electrons, the electrons and the trapped 'holes' will recombine. As a result, the metal colloid becomes smaller, the induced absorption is decreased. After UV irradiation has finished the destruction of the metal colloids becomes dominat and fading occurs.

FACTORS INFLUENCING THE PHOTOCHROMIC PROPERTIES

In order to get photochromic glasses with defined properties, for example defined amount of induced absorption, darkening and fading rate, it is necessary to 'optimize' all factors which influence photochromic properties. For simplicity's sake, photochromic properties are characterized by transmission before irradiation τ_0, by darkening after an irradiation of 5 min $\Delta\tau$ (this is the difference between τ_0 and τ_E, the transmission after irradiation) and by so-called half-life time of fading (the time which is necessary to reach the middle between τ_0 and τ_E again).

Photochromic properties mainly depend on the kind - AgX or CuX, (X^-: Cl^-, Br^-) - and of the structure of the microcrystals, this means on the structural and chemical disorder. In Table I a survey is given over the effects of different additional minor components which cause chemical disorder.

Glasses doped with Cu^+, Cd^{2+}, Sn^{2+} and X^- are selected from among the systems mentioned in Table 1. The advantage of this type of silverfree photochromic glass is the pronounced surface darkening[3]. It results from the excitonic absorption of the CuX microcrystals, which is shown in Figure 1. It follows from this, that darkening is nearly independent from sample thickness.

TABLE I Description of properties of different types of photochromic glasses.

Activator	Additive	Level of darkening	Thermal fading rate
AgX	Cu^+	medium	very fast
	Cu^+, Tl^+	strong	fast
CuX	Cd^{2+}	medium	slow
	Cd^{2+}, Sn^{2+}	medium, on surface: **strong**	slow
	Sn^{2+}	weak	very slow
	Tl^+, Sn^{2+}	weak	very slow

Photochromic properties depend on size of the microcrystals as well. Most applications demand a strong induced absorption and a fast fading simultaneously. But this goal is difficult to achieve because this is virtually a contradiction in terms. Larger microcrystals promote a strong darkening, but decrease the fading rate. Vice versa, smaller crystals result in decreased darkening, but fading rate is increased.

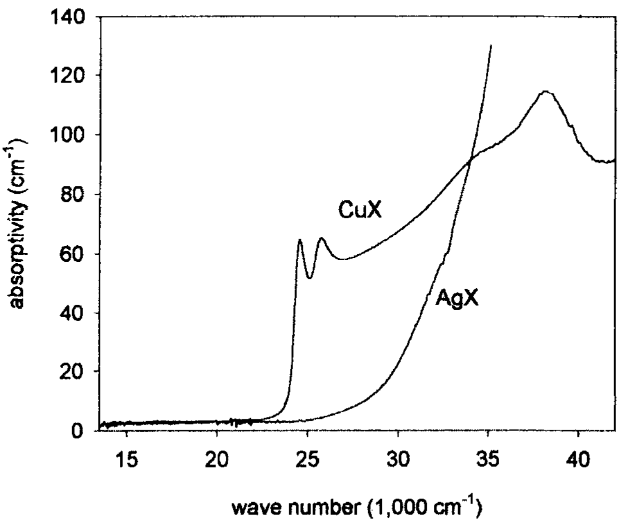

FIGURE 1 Absorption spectra of photochromic glasses containing AgX or CuX

Some factors should be mentioned which are related to the size of the microcrystals and influence darkening and fading: i) The traps for the 'holes' are situated within the crystals. ii) Sensitivity centers, these are preferential sites where nuclei for the metal colloids are formed, are on the surface of the crystal and compete against each other until one nucleus becomes bigger than critical. iii) The matter transport takes place via the surface of the crystal. iv) In smaller crystals the distance between trapped 'holes' and metal colloid is shorter than in larger ones.

IMPROVEMENT OF PHOTOCHROMIC PROPERTIES

The first idea we tried to improve the photochromic properties was to increase the chemical disorder. It is known from the photographic process that S^{2-} ions are used to control the properties of photographic films[4]. S^{2-} was introduced by addition of small amounts of CdS to the glass batch. The doped glasses show an increased darkening compared to samples without S^{2-} provided that crystal size is the same in both materials.

The most important finding was, however, that the addition of S^{2-} increases drastically the number and, for that reason, decreases the size of microcrystals compared to samples without S^{2-} after same heat treatment[5]. This is due to the effect of S^{2-} as a nucleating agent. Samples of glasses with and without S^{2-} were heat treated at temperatures between 470 and 570 °C for 60 min to develop the nuclei and then for 15 min at 600 °C to grow crystals. In Table II the number of crystals is given as a function of nucleation temperature. It is obvoius that the addition of S^{2-} clearly results in much more crystals than in glasses without S^{2-}. S^{2-} ions reduce the Cu^+ to metallic Cu^0 during heat treatment and the Cu^0 atoms (or colloids) act as nuclei.

TABLE II Number of crystals N (10^{14} cm^{-3}) vs. nucleation temperature T

T (°)	470	480	490	500	510	520	530	540	560	570
N (with S^{2-})	1.54	3.58	10.24	3.93	2.32	2.05	1.89	1.71	1.71	1.37
N (without)		0.05	0.13	0.17	0.06	0.04	0.02	0.01		

Next, we studied the influence of Cd^{2+} concentration, $[Cd^{2+}]$, on photochromic properties. Size, number and volume fraction of doped CuX microcrystals strongly depends on $[Cd^{2+}]$, Table III. Above 0,08 wt.-% Cd^{2+} (by chemical analysis) the volume fraction and the number of CuX microcrystals is increased, whereas the size is decreased.

Fortunately, the photochromic properties depend on [Cd^{2+}], too, Figure 2. The already known connection between increased darkening and decreased fading rate was found up to 0.08 wt.-% Cd^{2+}. But above 0.08 wt.-% we got samples with high darkening level and fairly fast fading. Thus, it is possible to improve both darkening level and fading rate by increasing the [Cd^{2+}]. This results in smaller CuX microcrystals with a higher chemical disorder caused by the incorporation of Cd^{2+} ions, as was shown by x-ray diffraction measurements.

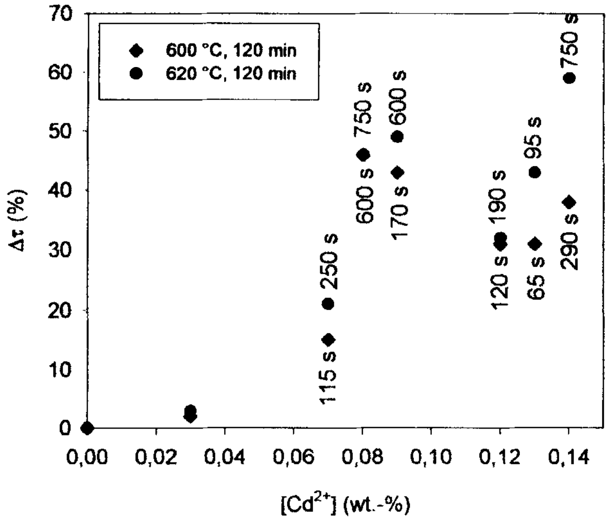

FIGURE 2 Darkening level and fading rate as a function of [Cd^{2+}]

TABLE III Influence of [Cd^{2+}] on formation of CuX microcrystals

[Cd^{2+}] (wt.-%)	Volume fraction CuX (vol.-%)	Diameter (nm)	Number of microcrystals (10^{13} cm^{-3})
0.00	0.019	29.5	1.33
0.03	0.021	31.6	1.87
0.07	0.023	35.0	2.05
0.08	0.025	52.6	2.40
0.09	0.043	46.0	2.90
0.12	0.046	40.7	13.20
0.13	0.048	33.2	20.20
0.14	0.049	23.2	25.90

The combination of the effects of S^{2-} and Cd^{2+} on photochromic properties resulted in glasses which show both a high darkening level and a fairly fast fading. Together with a further adjustment of the $[Cl^-]$ to $[Br^-]$ ratio we finally got an optimized silverfree photochromic glass with a transmission before irradiation $\tau_0 = 90$ %, a darkening after 5 min irradiation $\Delta\tau = 60$ % and a good fading rate, $t_{F/2} = 240$ s.

SURVEY ON SOME OTHER WAYS TO TAILOR PROPERTIES

Due to the shape of the induced absorption spectra of silverfree photochromic glasses, Figure 3, the color of the darkened glasses is greenish grey. For the use as sunglasses a brown or grey color is necessary without any green shade. The color of the silverfree glasses is corrected by adding of small amounts of noble metals. For example, 0.05 wt.-% Ag^+ or Pd^{2+} resulted in a grey color and did not affect the photochromic effect of the glasses. Probably, this is due to the incorporation of Ag or Pt atoms in the Cu colloids formed during darkening or, in case of Ag^+, to the formation of Ag and Cu colloids.

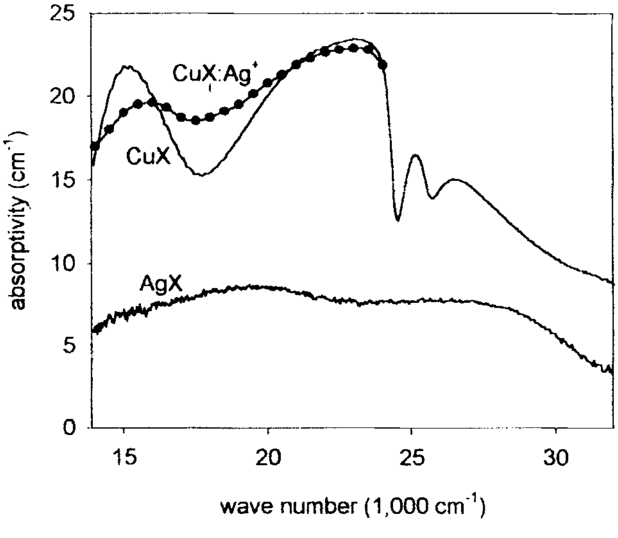

FIGURE 3 Absorption spectra of darkened photochromic glasses

The level of darkening is drastically increased when P_2O_5 (< 3 wt.-%) is added to the glass batch. Glasses modified in this way darken to a transmission after irradiation, τ_F, of less than 10%. Obviously, fading becomes very slow. The effect of P_2O_5 is that solubility of all components of the active microcrystals is decreased. This increases the amount of precipitated CuX microcrystals doped with Cd^{2+}. A further decrease in fading rate is possible by addition of 0.5 wt.-% WO_3. We darkened such glasses with an electron beam of a scanning electron microscope and created a series of fine lines and other geometrical figures. Observing the pattern by a microscope enlarged 1,000fold we found only straigt lines and area without any screening.

Glasses with completely different properties result if the network modifier oxide (NMO) concentration of the glass matrix is increased. This was done to increase the halide concentration in the glass. But the increase of the basicity of the matrix glass causes a competion between the halide and the oxygen ions for the cupous ions to happen. Finally, if basicity exceeds a certain level, the formation of CuX microcrystals is replaced by the formation of Cu_2O/Cu microcrystals. After heat treatment the obtained glasses are red, so-called 'copper ruby glasses'.

The characteristic absorption bands of the CuX microcrystals are vanished, but a sharp new band of the Cu_2O/Cu microcrystals arises. This band shows the typical behaviour of semiconductor microcrystals bands[6]. Peak maximum position depends on size of the microcrystals. Pumping of this absorption band by a laser results in an absorption saturation, the intensity of the absorption band decreases. A 'spectral hole' was burned, with the consequence that refractive index in this spectral range is affected by the laser.

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