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COMPARISON OF PHOTOCHROMIC GLASSES BY DARKENING AND FADING SPECTRA

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Abstract Darkening and fading spectra of different types of photochromic glasses are compared and reaction schemes are discussed.

INTRODUCTION

A great variety of photochromic glasses is known which differ in matrix glass systems, in activating components and, of course, in properties. Darkening and fading spectra are necessary to understand the corresponding processes and to improve and control the properties of the glasses.

EXPERIMENTAL

A diode array spectrometer was used to record the UV-vis absorption spectra of different types of photochromic glasses during darkening and fading. This spectrometer provides a high registration rate: each of the spectra is accumulated 20 times within 0.4 s. The glasses were irradiated and the spectra simultaneously recorded.

We investigated different types of photochromic glasses including experimental and commercial silver containing (AgX) and silverfree (CuX) glasses from Germany and Russia: i) glasses containing silver halides ($Ag(Cl_xBr_{1-x}):Cu^+$), HELIOVAR II^R type, ii) glasses containing cuprous halides ($Cu(Cl_xBr_{1-x}):Cd^{2+}$)[1], and iii) glasses activated with ($CuCl:Sb_2O_3$, Sn^{2+})[2] (Russian FKhS7 type).

The induced absorption by irradiation is small compared with matrix glass absorption. Thus, spectra of additional absorption are shown, this is the difference between the absorption during darkening or fading and the absorption before irradiation. These spectra show the changes of absorption only.

DARKENING AND FADING SPECTRA

Spectra of glasses containing $Ag(Cl_xBr_{1-x})$ microcrystals show only a strong UV absorption band which is a superposition of the absorption of the AgX crystals and of the UV absorption edge of the matrix glass, Figure 1. Absorption spectra of glasses containing $Cu(Cl_xBr_{1-x})$ microcrystals always show the two exciton absorption peaks of the CuX microcrystals around 25,000 cm^{-1}. Position of the exciton absorption peaks depends on size and the distance between the maxima of the two peaks depends on the Cl^-:Br^- ratio.

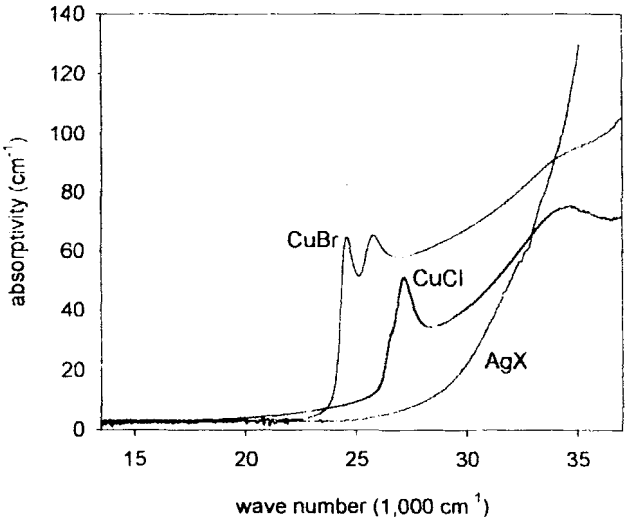

FIGURE 1 Absorption spectra of photochromic glasses containing AgX or CuX

Heliovar II[R]

Irradiation causes the induced absorption to arise. Spectra during darkening are given in Figure 2. The spectra is composed of three single bands, which appeare at about 16,000, 21,000 and 28,000 cm^{-1}. The growth rate of the bands is comparable. The origin of the bands are the silver colliods wich are formed during darkening on the surface of the microcrystals. A more detailed analysis of the spectra shows that the band at about 21,000 cm^{-1} does not change the position during darkening. The maximum of the band at 16,000 cm^{-1} is shifted towards higher wave numbers, the maximum of the band at 28,000 cm^{-1} is shifted to lower wave numbers. Position of both bands depends on shape of the

colloid. The shift is the result of the formation of oblate silver colloids[3]. The central band represents the part of colloid absorption which does not depend on shape.

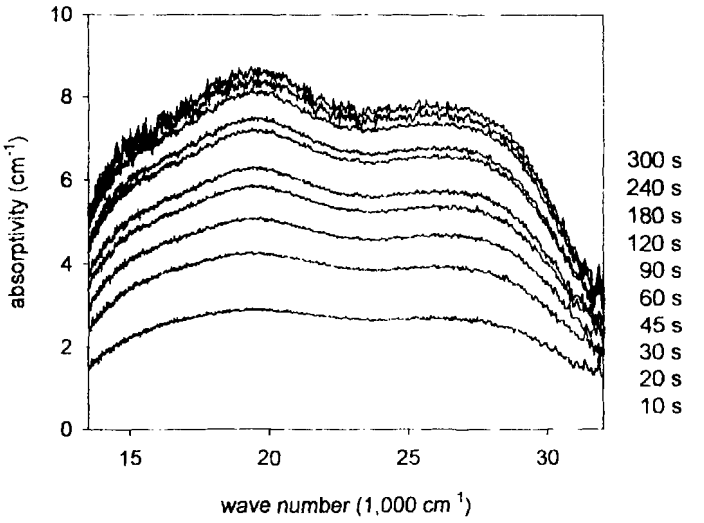

FIGURE 2 Additional absorption during darkening of HELIOVAR II[R]

Fading spectra of the same glass are shown in Figure 3. During fading the decrease of intensity of the three bands is varying rate. The band at about 16,000 cm^{-1} decreases fast whereas the other two bands decrease slower. This is found with all AgX activated photochromic glasses.

Copper-Cadmium-Halide photochromic glasses

The changes in absorption spectra during darkening are more pronounced for these glasses compared with the AgX containing glasses discussed above. Additional absorption spectra for different darkening times are given in Figure 4. The narrow band at about 16,000 cm^{-1} is shifted towards lower wave numbers during darkening.

The main feature is the broad absorption area around 25,000 cm^{-1}. It shows a more complex structure. The two sharp minima arise at exactly the same positions where the maxima of the exciton bands are. The intensity of the exciton absorption bands before is higher then after irradiation. This is due to the decrease of concentration of excitons during darkening. The concentration is increased again during fading. However, the main

part of this area is a broad band at about 23,000 cm^{-1} which results from the absorption of copper colloids. It represents the colloid absorption that is not affected by shape of the colloids. At about 31,000 cm^{-1} a weak band is found. It is shifted during darkening towards higher wave numbers. This band together with the band at 16,000 cm^{-1} represents the colloid absorption that depends on the shape of the colloids.

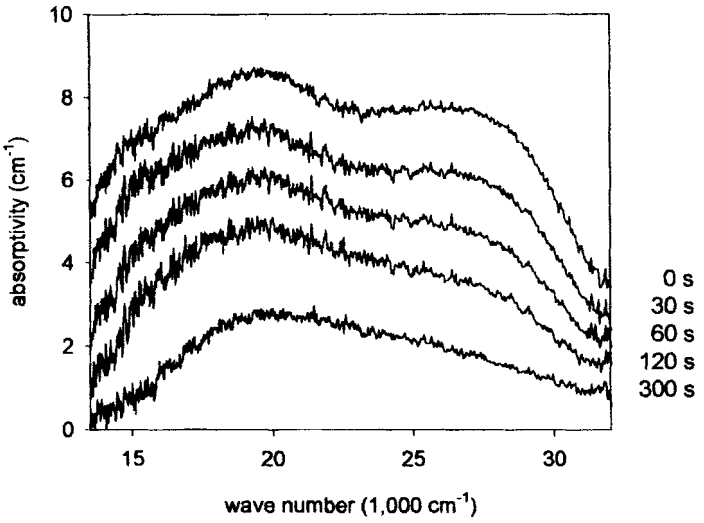

FIGURE 3 Additional absorption spectra during fading of HELIOVAR II^R

Changes at about 40,000 cm^{-1} are connected with the $d^{10} \rightarrow d^9s^1$ transition of Cu^+.

During fading all bands disappeare with nearly the same rate. The spectra show the same shape as the corresponding spectra recorded during darkening. This is the main difference between the AgX and the CuX containing photochromic glasses.

The pronounced surface darkening of the copper-cadmium-halide photochromic glasses is due to the exciton absorption bands, Figure 1. The UV radiation interacts stronger then in case of AgX containing photochromic glasses. The CuX containing glasses darken in a 0.2 to 0.3 mm thin surface layer, but absorptivity is more then twice the absorptivity of the AgX containing glasses. It seems that induced absorption does not depend on sample thickness. In this case a spectacle lens uniformly turns dark. The AgX containing glasses darkens more, but color depends on sample thickness. This may be a problem when lenses with high curvature are necessary.

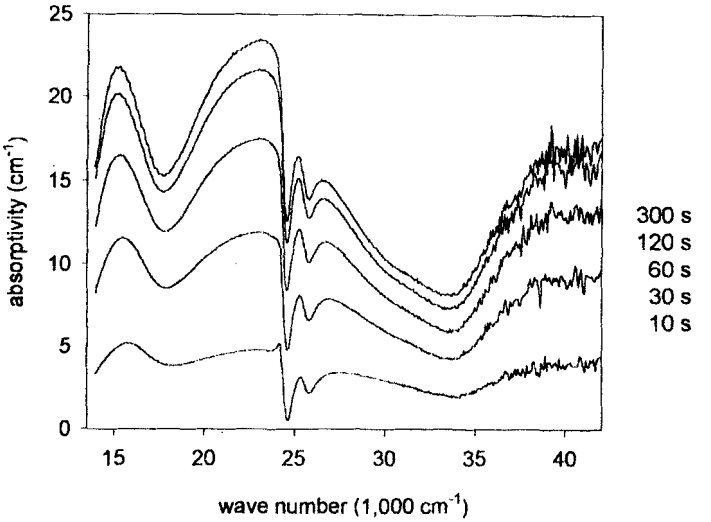

FIGURE 4 Additional absorption spectra during darkening of a CuX containing glass

FKhS7 type glasses

Glasses of this type show the same behaviour as the glasses discussed above. Due to the CuCl microcrystals the exciton absorption bands are shifted to about 27,000 cm^{-1}. The darkening is smaller and the fading is slower then in the CuBr:Cd^{2+} activated glasses.

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