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Silver halide-containing photochromic powders of SiO_2 sol–gel glass

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In order to develop a photochromic powder, an SiO_2-gel based on tetraethoxysilane (TEOS) was doped with $AgNO_3$ or $AgNO_2$. The dried gel pieces were pulverized and treated with aqueous or ethanolic halide solutions for growing silver halide microcrystals. Both the introduction of cuprous compounds such as CuBr, CuCl, Cu_2O, $Cu(CH_3COO)_2 \cdot H_2O$ or sulphur-containing compounds and the formation of $AgBr_xCl_{1-x}$ crystals lead to variations of photochromic properties. X-ray diffraction measurements indicate that the average diameters of silver halide microcrystals are limited to 70–110 nm. Ultraviolet–visible spectroscopic investigations show the reversibility of the darkening/fading process. Cu^+-containing samples exhibit a remarkable fading even at room temperature.

1. Introduction

It is relatively simple task to prepare a material with photosensitive behaviour; silver halide crystals finely divided in a transparent matrix are sufficient. But the preparation of a photochromic system is connected with a series of problems.

From the experiences of developing of photochromic glasses [1–6], the authors realized that there are several demands on a photochromic system.

(i) The photochromic crystals have to be included in an inert matrix system, for instance without double bonds, reactive groups and residues of solvents, to prevent the irreversible bonding of products of the irradiation process or their diffusion into the matrix system.

(ii) To exhibit photochromic behaviour, the possible crystals of AgBr, AgCl, CuBr or CuCl should have an optimal size of about 10–50 nm. With increasing size, the photosensitivity of crystals rises but reversibility disappears.. Hence the task is to stop uncontrolled growth of the crystals.

(iii) A good photochromic characteristic is only due to disordered microcrystals. Both the degree of Frenkel-disorder and of the introduction of foreign ions, influence the photochromic properties. In particular, the introduction of ions such as Cu^+, S^{2-}, Cd^{2+}, Ti^+, Pb^{2+} and the formation of crystals of $AgBr_xCl_{1-x}$, e.g. the exchange of some of the bromide ions by chloride ions, is desirable.

This report is concerned with precipitation of microcrystals, the coactivation process (e.g. the introduction of foreign ions) and the formation of mixed crystals in glass powders derived from the sol–gel process.

Such powders, or also thin films, produced by the sol–gel route show some advantages in relation to photochromic glasses. They can serve as a subsequent treatment of glassy or other surfaces. In comparison to glasses, it is not necessary to stabilize halide ions at such high temperatures, like in the melting process (about 1450 °C). Therefore, it is possible to increase the silver halide concentration markedly and to vary the composition of the matrix system in a wide range, dependent on the matrix properties desired.

2. Experimental procedure

2.1. Gel synthesis

A gel based on tetraethoxysilane (TEOS) was chosen as the matrix system for the investigations. This system allows us to concentrate on effects made by the minor components. For applications of these materials it is useful to modify the matrix system by drying control chemical additives (DCCA), network modifiers and ormocers for decreasing the drying temperature and for adapting the refractive index, hardness, ultraviolet transmission, thickness of layers and hydrolytic class.

The SiO_2 gels normally were synthesized from TEOS, ethanol, H_2O and 1 M HNO_3, where the molar H_2O/TEOS ratio ranged from 4–10 (here 4), the ethanol/TEOS ratio from 1–4 (1) and the HNO_3/TEOS ratio from 0.03–0.07 (0.07), leading to gelation times of 15–100 h (15) at 50 °C. Ag^+ ions were introduced as $AgNO_3$ or $AgNO_2$ in solution with a part of the ethanol. The concentration varied from 0.2–4.2 wt % Ag^+ in relation to SiO_2 (1.56 wt % for the present investigations). With that it reaches values about 50 times greater than in conventional glasses. After stirring for 30 min, the sols gelled at 50 °C and then were dried at 30 °C for 1 week. The clear, dry gel pieces were pulverized. Some of the samples are heat treated up to 400 °C, in order to investigate the effect of burning out of the organics and the influence of

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temperature on the growth process of the microcrystals.

2.2. Diffusion process

To develop microcrystals of AgBr or AgCl the powders or thin films undergo a diffusion process. To investigate the conditions of precipitation of silver halide microcrystals, pulverized samples (0.2 g) of dried, 1.56 wt % Ag^+ (as $AgNO_3$) containing gels are stirred with 10 ml ·0.1 M hydrous NaBr solutions, normally for 2 h at room temperature. The following experimental conditions were varied.

(i) Variation of the cation (0.1 M solutions of NaBr, NaCl, KBr, KCl, NH_4Br and NH_4Cl).

(ii) Variation of the grain size of the gel powder (in three steps: $\leqslant 160$ µm, 160–250 µm, 250–500 µm).

(iii) Variation of temperature (25, 40, 60, 75, 95 °C).

(iv) Variation of time (10, 40, 60, 120, 480 min).

(v) Use of gaseous HCl or HBr.

The gel powders were exposed to a saturated atmosphere of HCl or HBr for 8 h.

2.3. Precipitation of $AgBr_xCl_{1-x}$ crystals

The experimental details for the precipitation of mixed crystals were as follows:

(i) using of an equimolar mixture of 0.1 M NaCl and 0.1 M NaBr solution, variation of the diffusion time (5 min to 2 h);

(ii) treating of the gel with (1) 0.1 M NaCl solution for 2 h, washing and drying, and then with (2) 0.1 M NaBr solution under variation of experimental time (5 min to 2 h).

At first the ratio of Ag:Cl was set at 1:5 and that of Ag:Br at 1:28.

(iii) variation of the Ag:Br and Ag:Cl ratios: (1) Ag:Cl = 1:50 and Ag:Br = 1:1; (2) Ag:Cl = 1:50 and Ag:Br = 1:0.25.

For drawing of a comparison, some of the samples were only treated with 0.1 M aqueous solutions of NaCl.

2.4. Coactivation with Cu^+ ions

To introduce copper compounds into the gel materials, two experimental methods were favoured:

(i) treating of dried, AgBr or AgCl crystal containing gels with hydrous or ethanolic solutions of CuBr/CuCl or Cu_2O, stirring at room temperature for 2 h, washing and drying;

(ii) direct introduction of copper compounds (as Cu_2O or $Cu(CH_3COO)_2 \cdot H_2O$) in the sol synthesis. The concentration relations between silver and copper ranged from 1:0.1 to 1:1.

The temperature of the sol synthesis was varied between 25 and 75 °C.

2.5. Introduction of sulphur compounds

In the sol soluble compounds like Na_2SO_{31} $(NH_4)_2S$ or KSCN were introduced for the sol synthesis, in each case with the molar ratio Ag:S = 1:0.01. After gelation and drying of the gels, they were exposed to a hydrous 0.1 M NaBr solution for 2 h.

2.6. X-ray diffraction measurements

X-ray diffraction measurements (XRD) were carried out with the X-ray diffractometer D5000 (Siemens). The particle size used was normally set to 250–500 µm.

2.7. Ultraviolet–visible (UV–VIS) spectroscopic investigations

The UV–VIS spectroscopic measurements were carried out with a photodiode array spectrometer L.O.T. Oriel (including analysing software InstaspecII). Powder samples were measured in the reflection mode (60° incidence direction); the Kubelka-Munk function $F(R_\infty)$ is plotted versus wave number.

$$K/S = F(R_\infty) = (1 - R_\infty)^2/2R_\infty \qquad (1)$$

with K the absorption coefficient, S the scattering coefficient, and R_∞, the diffuse reflection of an infinitely thick sample. Here the Kubelka-Munk function exhibits an analogous behaviour to absorption, because the scattering coefficient S is relatively constant within the measured wave number range.

For investigation of the darkening and fading, the samples were measured, then irradiated with a Xenon lamp (150 W) at a distance of 10 cm for 5 min. After irradiation they were measured again.

Darkening and fading at different temperatures was measured using a microscope heating stage (Linkam). This equipment is not suited for measuring powders in the reflection mode. Measurements are only practicable in the absorption mode and require transparent samples. The available gel piece samples always differ slightly in thickness. For that reason, in the absorbance versus wave number spectra, absorbance is always related to the sample thickness (cm^{-1}) (see Figs 5 and 6 below). So the spectra are directly comparable [7].

3. Results and discussion

3.1. Diffusion process

A comparison of 0.1 M solutions of NaBr, NaCl, KBr, KCl, NH_4Br and NH_4Cl shows that the amount of precipitated crystals of silver halide (AgHal) occurs in the order $Br^- > Cl^-$ and $Na^+ > K^+ > NH_4^+$. The diameter of the microcrystals is independent of the type of solution and ranges between about 70 and 110 nm.

If gels with varied particle sizes (160–500 µm) are treated with NaBr solution, the number microcrystals also increases with increasing surface per gram of gel, but the average diameter of AgBr crystals is not influenced.

The variation of temperature (from room temperature to 95 °C) gives the same behaviour: increasing the amount but not the diameter of the precipitated AgBr cyrstals.

To produce similar crystal diameters and concentrations, a very high concentration of gaseous HCl or HBr is necessary. In this way, surfaces of the gel particles were corroded by the acids.

It is possible to increase the precipitated amount of AgHal microcrystals with the methods mentioned above, but the diameters are limited to 70–110 nm. Hence it seems that the diameters are limited by the pore sizes in the gel and an increase in the amount of microcrystal is attributed to a diffusion into deeper layers of the gel.

3.2. AgBr$_x$Cl$_{1-x}$ crystals

Glasses with AgBr$_x$Cl$_{1-x}$ crystals in general exhibit more distinct photochromic properties than those with crystals of AgBr or AgCl (larger transmission changes, faster fading process). The causes of these effects seem to be a broadening of spectral sensitivity and a favourable impact of the disorder of the AgBr lattice by smaller chloride ions. The results of the examination of the precipitation conditions of AgBr$_x$Cl$_{1-x}$ crystals in the gel are given below.

If an equimolar mixture of NaCl and NaBr solution was used to treat the Ag$^+$-containing gels by variation of the time of treatment (5 min to 2 h), the results of the XRD analysis are similar. In each case, only AgBr crystals were detected.

In the next experiment, the gel was first treated with a NaCl solution. After washing and drying of the gel, it was treated with NaBr solution under variation of experimental time (5 min to 2 h) and variation of Ag : Br and Ag : Cl ratios (1) Ag : Cl = 1 : 5 and Ag : Br to 1 : 28, (2) Ag : Cl = 1 : 50 and Ag : Br = 1 : 1. We hoped for partial recrystallization of the previously precipitated AgCl crystals. Surprisingly, a time of 5 min is sufficient to recrystallize the precipitated AgCl crystals completely into AgBr (see Fig. 1).

The ratio of Ag : Cl = 1 : 50 was retained in the next experiment, but Ag : Br was decreased to 1 : 0.25. The X-ray diffractogram (see Fig. 2) contains peaks of AgCl, AgBr and many various mixed crystals AgBr$_x$Cl$_{1-x}$, especially a pronounced peak of AgBr$_{0.25}$Cl$_{0.75}$.

3.3. Coactivation with Cu$^+$ ions

Cuprous halides introduced in silver halide-containing photochromic glasses change the original AgHal lattice from the NaCl type partly into ZnS type, because the smaller, more covalent Cu$^+$ ions ($r_{\mathrm{Cu}^+} = 95$ pm, $r_{\mathrm{Ag}^+} = 113$ pm) occupy tetrahedral gaps of the NaCl type lattice. Such lattice defects lead to additional located levels in the band scheme and moreover increase the mobility of charge carriers. In this way small amounts of Cu$^+$ ions intensify the photochromic behaviour of the system.

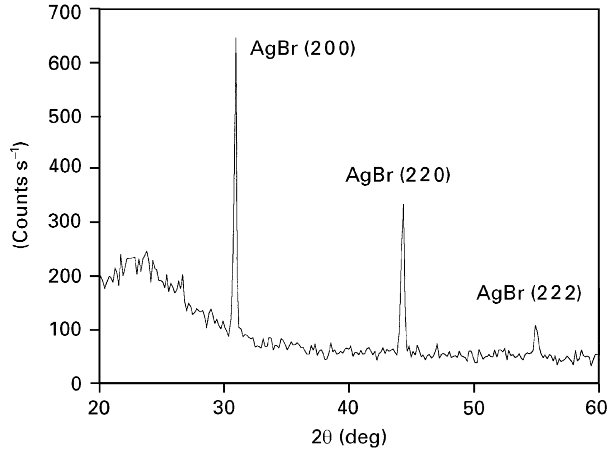


Figure 1 XRD pattern (sample: Ag : Cl = 1 : 50, Ag : Br = 1 : 1, 5 min in NaBr solution).

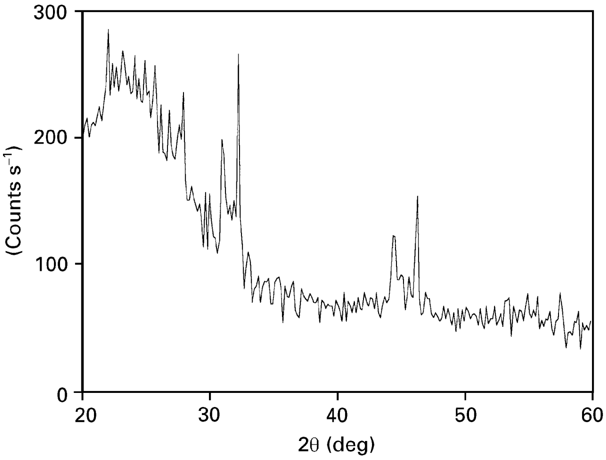


Figure 2 XRD pattern (sample: Ag : Cl = 1 : 50, Ag : Br = 1 : 0.25, 5 min in NaBr solution).

In glasses, Cu$^+$ ions are stabilized by the high melting temperatures, but it is a great problem to introduce Cu$^+$ ions in the gel. H_2O, contained in the sol, leads to oxidation and formation of $[Cu(H_2O)_6]^{2+}$ complexes. The reaction of Ag$^+$ and Cu$^+$ to Ag^0 and Cu^{2+} should be restricted by a bonding of Ag$^+$ ions to the network. A treatment of the AgBr or AgCl crystal-containing gels with aqueous or ethanolic solutions of a cuprous compound (such as CuBr/CuCl or Cu_2O) results in an oxidation of the Cu$^+$ ions to Cu^{2+}. The diffractograms show relics of insoluble Cu_2O in the gel and silver precipitation. A better way is the direct introduction of Cu$^+$ (as Cu_2O) or of $Cu(CH_3COO)_2 \cdot H_2O$ (with intermediate formation of small amounts of Cu$^+$ by reduction with ethanol) in the sol. Thereby no noticeable amount of silver is observable in the diffractograms. The investigations were carried out with different amount of Cu$^+$ and at different temperatures of sol-synthesis. Table I shows the results of XRD measurements of gel powders with Cu_2O as Cu$^+$ supplier. An increasing amount of Cu$^+$ (A, B, C) dissolved in the sol causes an increasing disorder of the precipitated AgBr crystals, probably by the introduction of Cu$^+$ ions into the tetrahedral gaps of the AgBr lattice, as is seen at the changed relative intensities of AgBr peaks compared to the ideal case. An increase in the temperature of synthesis has similar effects. The decrease of the average diameters with increasing amount of Cu$^+$ or temperature is also remarkable.

3.4. Coactivation with sulphur species

Sulphur compounds, for instance CdS or Cu_2S, show a favourable effect on photochromism, if very small

TABLE I Average diameters and relative intensities (XRD results at $AgBr/Cu_2O$ containing gel powders)

Sample	Ratio of $Ag^+:Cu^+$	Temperature of sol synthesis (°C)	Average diameter of AgBr crystals (nm)	Relative intensities of AgBr peaks		
				(200) (%)	(220) (%)	(222) (%)
A	1:0.1	25	112	100	54	17
B	1:0.2	25	98	100	54	20
C	1:1	25	85	100	92	10
D	1:0.1	40	108	100	54	17
E	1:0.1	60	99	100	59	19
F	1:0.1	75	97	100	67	21
$AgBr_{ideal}$				100	56	16

amounts of them (up to amounts equal to about 1/100 Ag^+) are introduced into the glass batch. First, the bivalent S^{2-} ions lead to a pronounced disturbance in the anion part of the lattice with similar consequences as Cu^+ ions, as mentioned above. Second, sulphur compounds cause a nucleation effect on the precipitation of AgHal or CuHal crystals. Therefore, many very small disordered crystals are formed, resulting in an improved photochromism: increased darkening and faster fading process [3]. To transfer this to gels, in sol soluble compounds like Na_2SO_3, $(NH_4)_2S$ or KSCN were introduced in the sol synthesis, in each case with the molar ratio Ag:S = 1:0.01. After treating the dried gels with aqueous NaBr solution, only AgBr crystals could be detected by XRD. The resulting diameters and relative intensities as an expression of the disorder of the crystals are shown at Table II. The average diameters are not influenced; thus the expected nucleation effect of the sulphur compounds does not occur.

3.5. UV–VIS spectroscopic investigations

The $F(R_\infty)$ versus wave number spectra show three distinct absorption bands. The peak at about 24000 cm^{-1} results from colloids of silver (size about 1–3 nm diameter), sitting on the surface of AgBr crystals. At oblate ellipsoids of colloidal silver specks, this peak splits into two other absorption peaks. The ellipsoid with the rotation axis parallel to the electrical field vector has an absorption peak at about 32000 cm^{-1}, and perpendicular to the electrical field vector the peak lies at 18000 cm^{-1} [8].

Fig. 3 shows the $F(R_\infty)$ function of 5 min irradiated samples with $Cu(CH_3COO)_2 \cdot H_2O$, whereas sample J is distinguished by a molar ratio Ag:Cu = 1:0.1; sample K by Ag:Cu = 1:0.2 and sample L by Ag:Cu = 1:1. The spectra were analysed with the PEAK-FIT program; results are shown in Table III. With increasing amount of $Cu^{+/2+}$ the peaks at about 18000 and 24000 cm^{-1} are shifted to greater wave numbers, whereas the peak at about 32000 cm^{-1} is not influenced by the $Cu^{+/2+}$ concentration. The realized darkening levels increase with $Cu^{+/2+}$ concentration; thus the disordering of the AgBr crystals by cuprous ions leads to an improvement of darkening. The small decrease in darkening at wave numbers below about 18000 cm^{-1} results from the shift of the peaks at about 18000 cm^{-1} and 24000^{-1} to higher wave numbers with increasing copper concentration. Fig. 4 contains the difference spectra before and after 5 min irradiation of the samples J, K and L. Despite the not really controlled initial state before irradiation (the possibility of a slight exposure to sun light), these spectra of the additional photochromic absorption exhibit a similar behaviour, such as the irradiation spectra in Fig. 3.

TABLE II Average diameters and relative intensities (sulphur-containing gels)

Sample	Sulphur compound	Average diameter of AgBr crystals (nm)	Relative intensities of AgBr peaks		
			(200) (%)	(220) (%)	(222) (%)
G	Na_2SO_3	100	100	70	25
H	$(NH_4)_2S$	91	100	62	12
I	KSCN	105	100	64	12

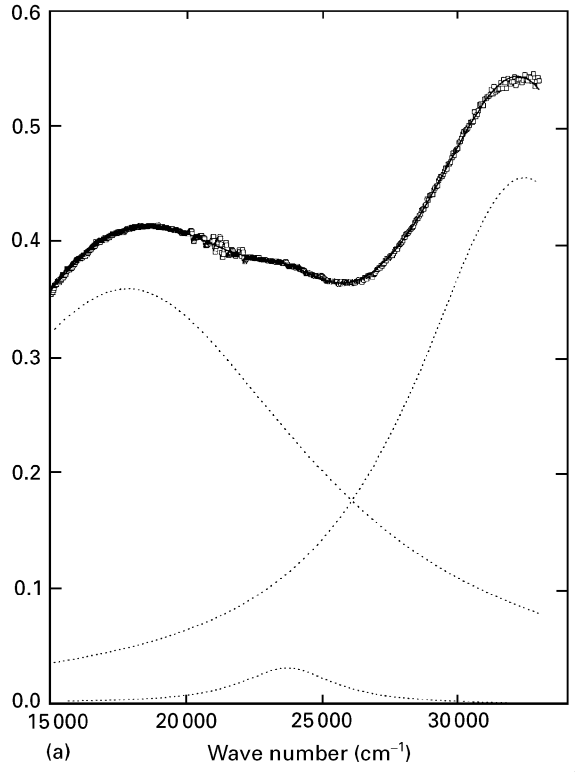
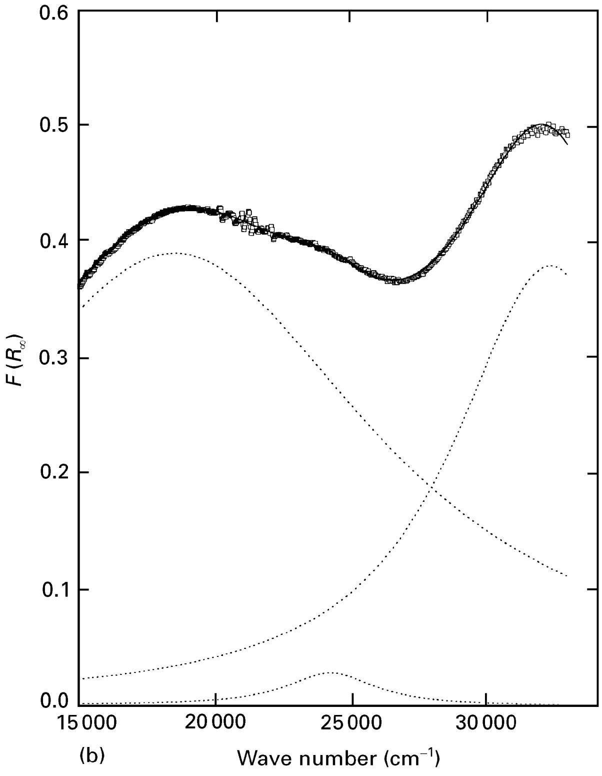


Figure 3 UV–VIS spectra of irradiated samples with $Cu(CH_3COO)_2 \cdot H_2O$: (a) sample J, Ag:Cu = 1:0.1; (b) sample K, Ag:Cu = 1:0.2; (c) sample L, Ag:Cu = 1:1.



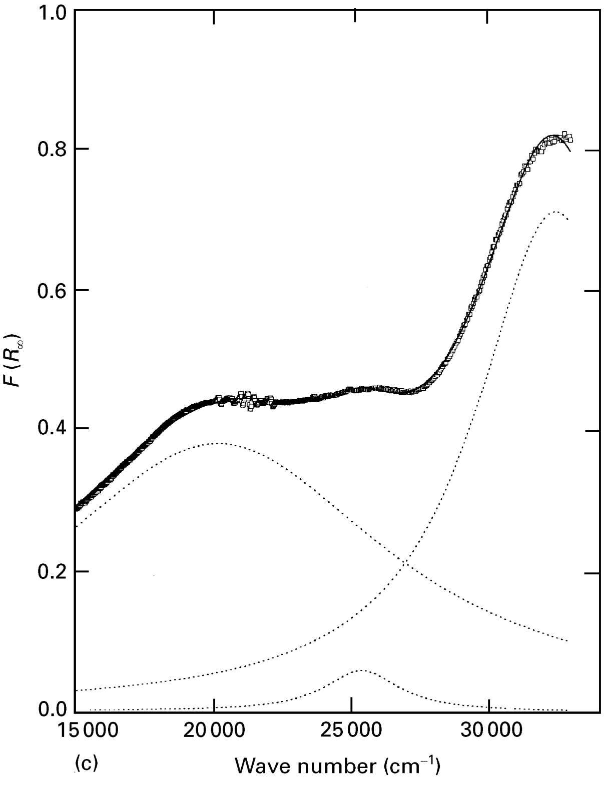


Figure 3 (continued)

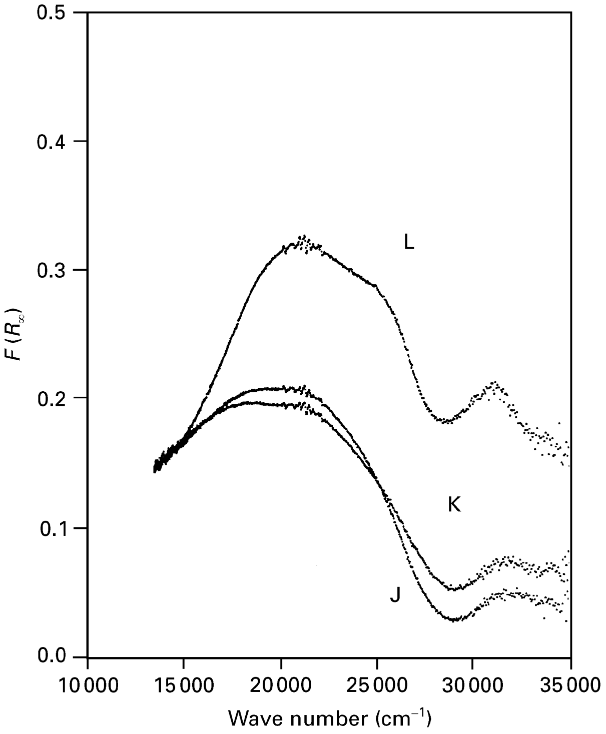


Figure 4 Difference by irradiation (samples J, K, L).

The darkening and fading processes of sample K are measured on the above-mentioned gel piece. The darkening was carried out at room temperature. Fig. 5 shows spectra recorded at different times; Fig. 6 contains spectra of the fading process. During fading, the sample was heated up to 200 °C at a rate of 5 K min^{-1}. The greatest changes occur in the temperature range 100–150 °C. At about 150 °C the fading process is nearly terminated.

Time-dependent measurements at different fading temperatures of the same sample are shown in Figs 7–9. The first spectrum was taken after 5 min irradiation. Then the sample was heated up to 100, 120 and 150 °C, respectively, at a rate of 40 K min^{-1}. On reaching the measuring temperature, the second spectrum was recorded and then spectra were taken each minute (until whole bleaching). It is interesting to note that, also at room temperature, a distinct fading occurs. With increasing temperature the fading accelerates. At 100 °C the fading is completed within 15 min at 120 °C within 10 min, and at 150 °C within 2 min. The greatest changes occur during heating up and during the first minute at high temperature.

The reversibility of the darkening and fading process was considered by repeating nine times. After 3 min irradiation, the gel piece of sample K was heated to 150 °C at a rate of 40 K min^{-1}. The temperature was maintained constant for 3 min. After rapid cooling, the process started again. Fig. 10 shows spectra recorded after irradiation and Fig. 11 after 3 min at 150 °C. The first cycle differs from the other: it exhibits the deepest darkening level and the best fading, leading to a great difference by irradiation. Beginning with the second cycle, the process adjusts to one level; only the basic line rises. Consequently, the differences produced by irradiation (see Fig. 12) remain the same.

TABLE III Spectra calculation: centre wave numbers of peaks from Lorentz-type (5 min irradiated samples)

Sample	Centre wave number (cm^{-1})		
J	17 840	23 730	32 410
K	18 510	24 250	32 310
L	20 180	25 390	32 420

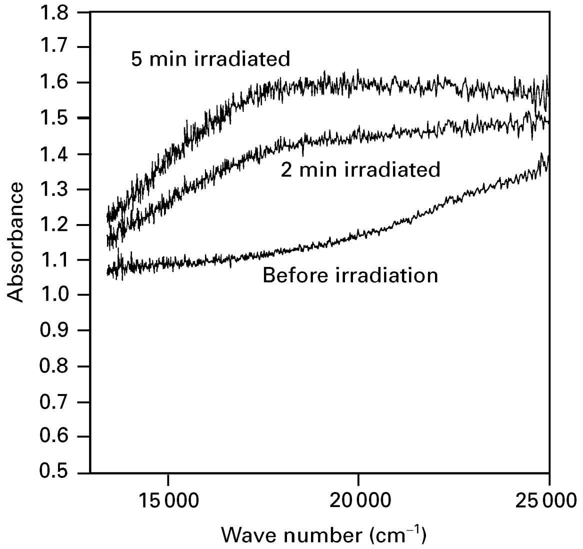


Figure 5 Darkening process, sample K.

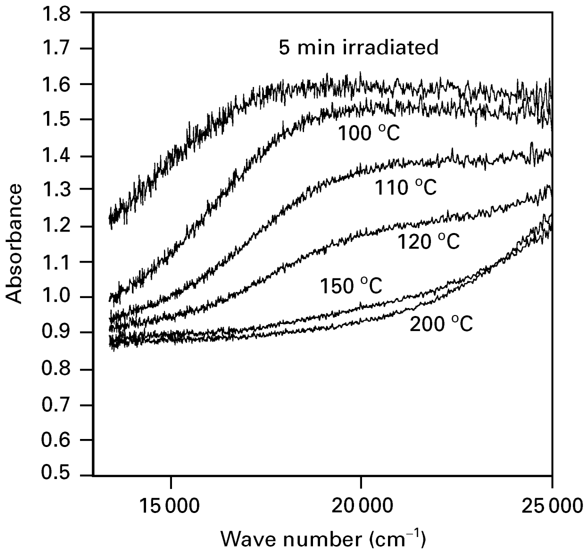


Figure 6 Fading process, sample K.

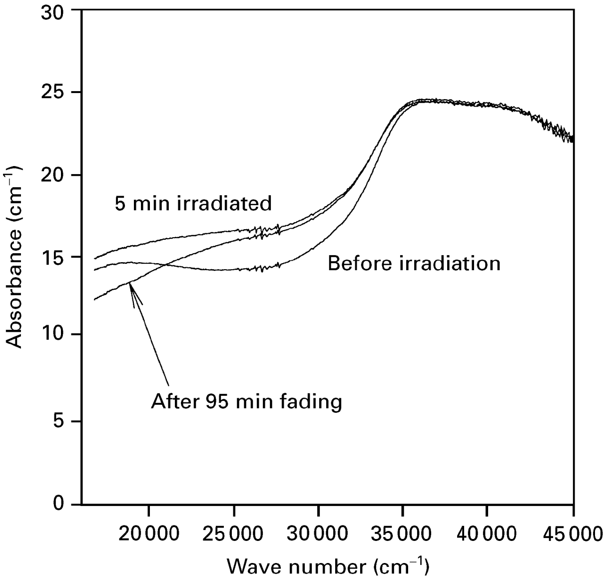


Figure 7 Fading process at 25 °C.

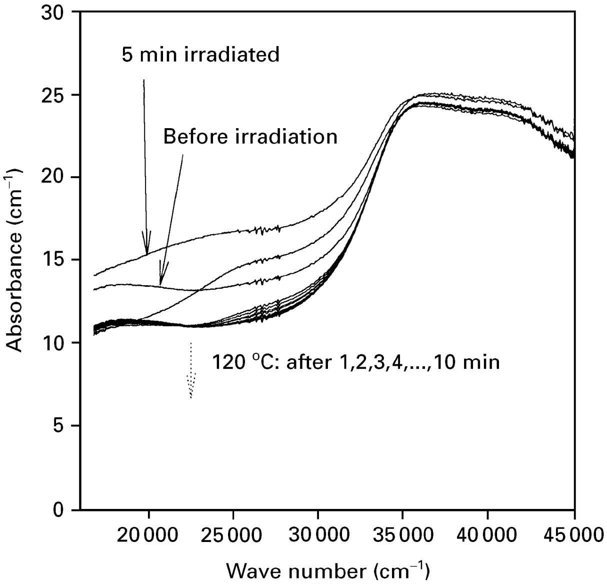


Figure 8 Fading process at 120 °C.

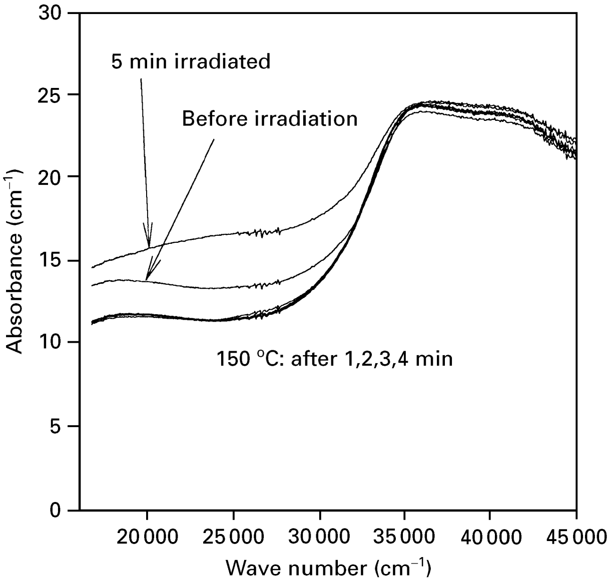


Figure 9 Fading process at 150 °C.

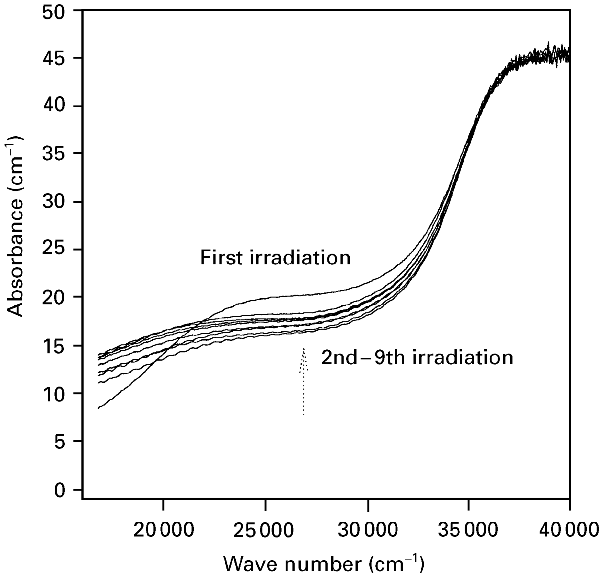


Figure 10 UV–VIS spectra of sample K after 3 min irradiation.

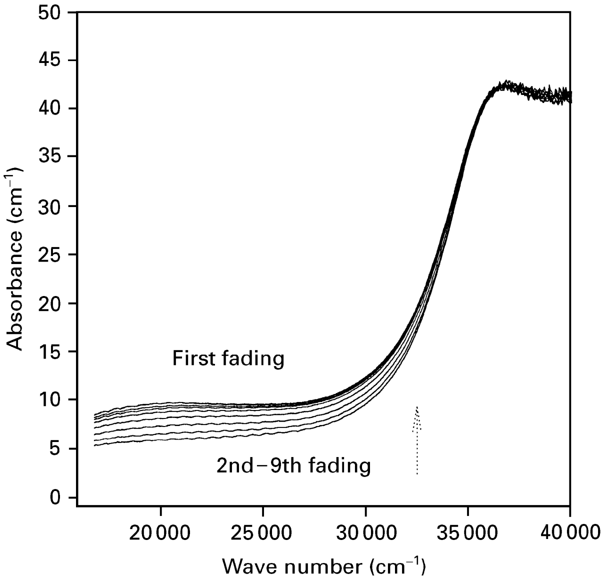


Figure 11 UV–VIS spectra of sample K after 3 min fading at 150 °C.

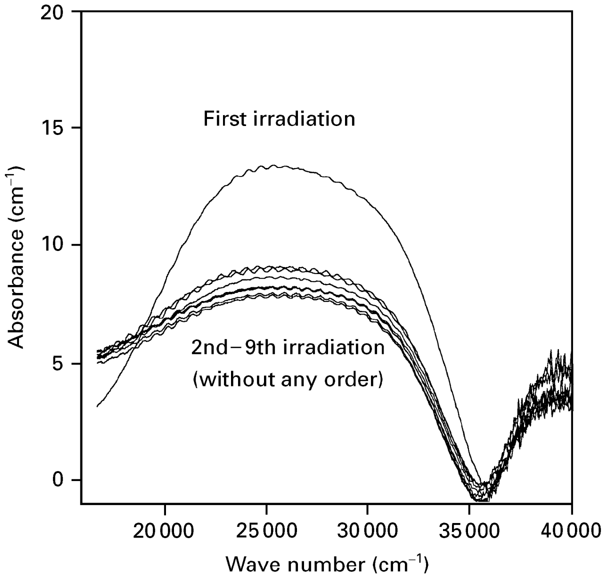


Figure 12 Difference by irradiation.

In general, measuring of the darkening behaviour of the powder samples demonstrates that the samples with $Cu(CH_3COO)_2 \cdot H_2O$ (and to a smaller degree with Cu_2O) in the sol exhibit the best photochromic properties. Dopants of sulphur compounds or the precipitation of $AgBr_xCl_{1-x}$ crystals only slightly improve the photochromic behaviour compared to the undoped case. AgBr-containing gel powders show a more pronounced darkening, than those with AgCl microcrystals, as can be seen in Fig. 13. This figure yields the difference spectra by a 5 min irradiation (reflection mode) of gel powders of a varied sample C (C_a, treated with 0.1 M NaBr solution; C_b, with 0.1 M NaCl solution; both, after washing and drying, heat treatment 280 °C/2 h + 400 °C/2 h).

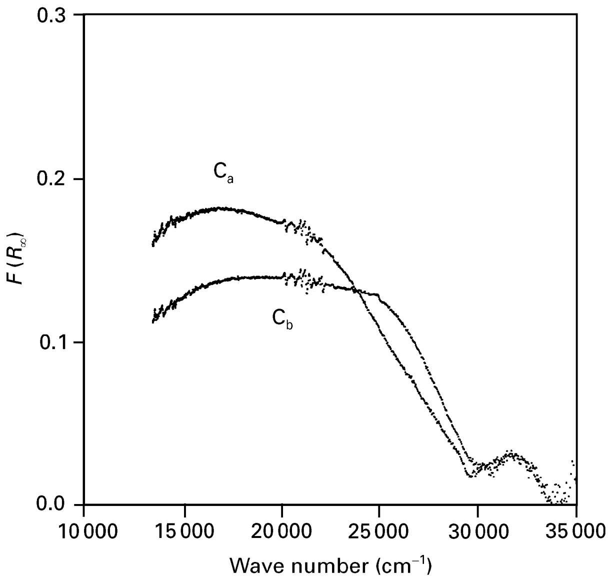


Figure 13 Difference by irradiation: sample C_a, C_b.

4. Conclusion

It is possible to synthesize photochromic gel powders by a treatment of Ag^+-containing SiO_2 gels with aqueous or ethanolic solutions of halide ions. Size and number of precipitated AgHal microcrystals are only slightly influenced by the conditions of treatment, such as temperature, time, size of gel grains, cations and concentration of the halide solution. The realized diameters of AgHal crystals assume values between 70 and 110 nm. Despite these relatively large diameters, the gel powders exhibit a pronounced photochromic behaviour. Sulphur compounds and the precipitation of mixed crystals $AgBr_xCl_{1-x}$ did not produce the expected effects on photochromism. By introduction of Cu^+ ions as coactivator, the powders show a deep darkening and a rapid fading at relatively low temperatures (100–150 °C). For the first time, fading at room temperature has been observed in gel glasses.

References

1. M. MULLER, D. PFEIFFER, A. KRILTZ and W. VOGEL, *Sov. J. Glass Phys. Chem.* **15** (1989) 324.
2. M. MULLER, J. VOIGT, A. KRILTZ and W. VOGEL, *Silikattechnik* **39** (1988) 221.
3. A. KRILTZ, *PhD thesis*, Friedr.-Schiller-University, Jena (1989).
4. A. KRILTZ and M. MÜLLER, *Silic. Ind.* **11–12** (1990) 343.
5. M. MÜLLER and H. REIß, *Jenaer Rundschau* **35** (1990) 36.
6. A. KRILTZ, M. MÜLLER and W. VOGEL, *Silikattechnik* **39** (1988) 423.
7. A. KRILTZ and M. MÜLLER, *Glastech. Ber. Glass Sci. Technol.* **67** (1994) 343.
8. A. A. ANIKIN and V. K. MALINOVSKY, *J. Non-Cryst. Solids* **34** (1979) 393.

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