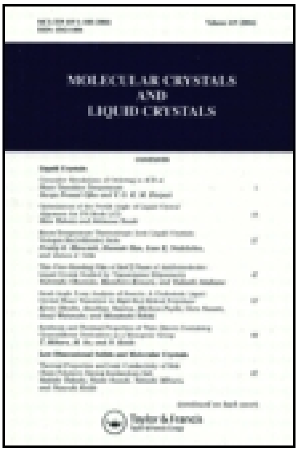

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High-Temperature UV-Vis Spectroscopic Investigations on the Second Annealing Process of Photochromic Glasses

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HIGH-TEMPERATURE UV-VIS SPECTROSCOPIC INVESTIGATIONS ON THE SECOND ANNEALING PROCESS OF PHOTOCHROMIC GLASSES

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Abstract A second annealing process of silver- or cuprous halide microcrystals containing glass changes their photochromic behaviour. The second annealing is carried out both below T_g of the glass and below the melting point of the crystals. In situ UV-VIS spectroscopic measurements in this temperature range indicate changes in excitonic peaks of CuBr or CuCl microcrystals as function of temperature, annealing time and cooling rate. Room temperature spectra of irradiated samples show a direct dependence on the conditions of the second annealing process. The decrease in the transition temperature of these small crystals below the bulk value causes partly transitions of the low temperature modification of the crystals into the high temperature modification, that does not contribute to excitonic absorptions and darkening ability.

INTRODUCTION

A first annealing at about 50 K to 200 K above T_g of the glass leads to nucleation and growing of the photochromic microcrystals. Temperature and time of annealing influence size, size distribution and number of precipitated microcrystals.[1-5] It is possible to modify the given photochromic properties by a second annealing step in the temperature range of about 250 °C to 400 °C, that means a heat treatment below T_g of the glass and also below melting and transition points of the crystals. The authors showed [10-12] that the melting points of such small crystals are decreased up to 200 K below the corresponding values of the bulk crystals. Melting of the crystals does not explain changes in photochromic properties by a second annealing. If glasses were heated up above such melting temperatures of microscopic crystals (for instance for spectroscopic measurements) and were rapidly cooled down, no change in photochromism was to be observed.

EXPERIMENTAL

For the investigations a glass of borosilicate type with 0.30 weight% Cu^{2+} (as CuO) and 4.17 weight% Br^- (as NaBr - sample A) or 1.85 weight% Cl^- (as NaCl - sample B) was chosen. The glasses were melted with a 400 g batch in a Pt crucible at 1450 °C for 4 h, including a stirring step of 30 min. After rapid quenching between copper plates to transformation range the glasses were cooled down from 550 °C to room temperature with a rate of about 4 $Kmin^{-1}$. A first heat treatment at 580 °C for 4 h leads to a developing of microcrystals with pronounced photochromism with an average diameter of 25 nm (A) and 114 nm (B) (measured by TEM). XRD was carried out at a D5000 SIEMENS diffractometer in step scanning mode. The spectra of 0.2 mm thick, polished samples were recorded at a photodiode array spectrometer (InstaSpecII, L.O.T.ORIEL) including a computer controlled microscope heating stage (LINKAM). For measuring photochromic properties, irradiation was carried out with UV light from a 150 W XBO lamp at room temperature (distance: 10 cm, time: 5 min). Spectra were taken directly before and after irradiation. [4, 10, 14]

INFLUENCE OF TEMPERATURE

Spectra were taken at room temperature, at a certain temperature (275 °C...475 °C) after a heating with 30 $Kmin^{-1}$, after 15 min at this temperature, after a rapid cooling (with about 100 $Kmin^{-1}$) at 40 °C and after 5 min at 30 °C. Some samples were also measured after 1.5 h at 25 °C. Then the measures were repeated (with new samples) with a slow cooling of 5 $Kmin^{-1}$. Figure 1 contains an example of a series of spectra. At 375 °C the excitonic peaks at about 27000 cm^{-1} or 25000 cm^{-1} are considerable decreased, even a bit more at 15 min at this temperature. After cooling the excitonic peaks recreate, but the intensity is not as high as before the second annealing. The comparison between 40 °C and 30 °C exhibits, that there is only a small hysteresis effect. A spectrum taken after 1.5 h at room temperature is not different to that at 30 °C (5 min). Such series of spectra were measured in the range from 275 °C to 475 °C. Figure 2 shows the differences in absorbance between the spectra taken before the second annealing and the spectra taken after 5 min at 30 °C (after the second annealing). From annealing temperatures of 275 °C to 375 °C the differences grow up, hence the absorbance is decreasing by the annealing process. Above 375 °C of annealing spectra approximate to the initial values. Figure 3 shows the absorbance of $z_{1/2}$-peak as function of annealing temperature (CuBr: $\tilde{\upsilon} = 24595$ cm^{-1}, CuCl: $\tilde{\upsilon} = 27125$ cm^{-1}) .

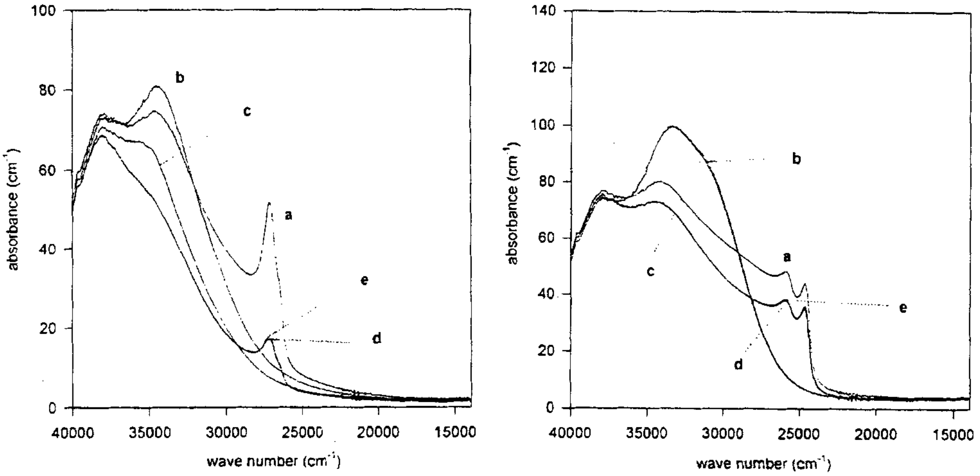

FIGURE 1: UV-VIS spectra during the second annealing process:
$T_{an} = 375$ °C, $v_{cool} = 100$ Kmin^{-1}, 1a: sample B 1b: sample A
a: before annealing (25 °C), b: at 375 °C, (heating rate: 30 Kmin^{-1}),
c: 15 min at 375 °C, d: after annealing: at 40 °C, e: 5 min at 30 °C

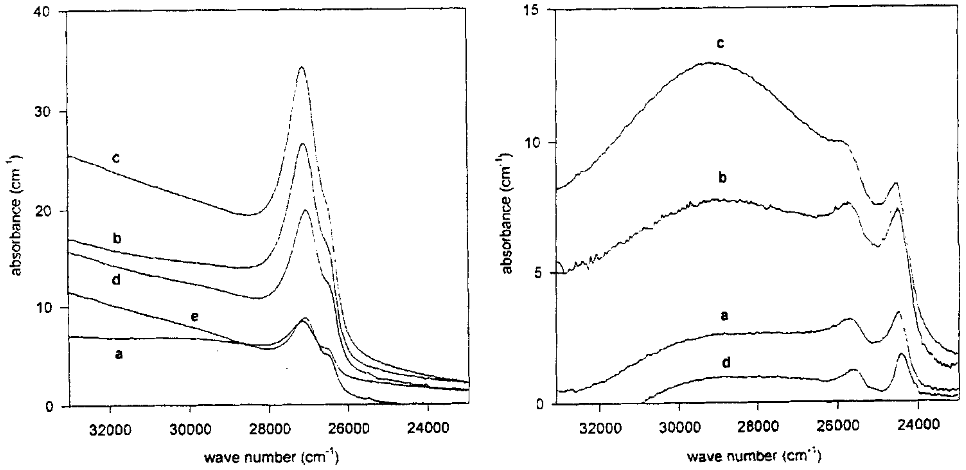

FIGURE 2: Spectral difference before and after a second annealing dependent on the temperature of the second annealing , 2a: sample B 2b: sample A
second annealing at: a: 275 °C, b: 325 °C, c: 375 °C, d: 425 °C, e: 475 °C

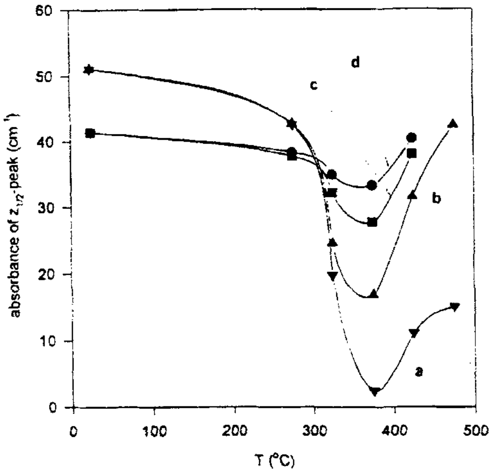

FIGURE 3: Absorbance of $z_{1/2}$-peak as function of the second annealing temperature (measured at room temperature) $t_{an} = 0.25$ h,
a: sample B, $v_{cool} = 5$ Kmin^{-1}, b: sample B, $v_{cool} = 100$ Kmin^{-1}
c: sample A, $v_{cool} = 5$ Kmin^{-1}, d: sample A, $v_{cool} = 100$ Kmin^{-1}

INFLUENCE OF COOLING RATE

Figure 4 contains graphs of absorbance of $z_{1/2}$-peak vs. cooling rate of CuBr (a) or CuCl (b) microcrystals containing samples. A lower cooling rate leads to a more distinct decrease of absorbance by the annealing process. With increasing annealing temperature the process is more dependent on the cooling rate. CuCl containing samples also show a more marked dependence on cooling rate, than CuBr containing samples.

INFLUENCE OF ANNEALING TIME

The influence of the time of the second annealing was investigated in the time range up to 4 hours (T = 325 oC, $v_{cool} = 100$ Kmin^{-1}). Because of the long time at high temperatures the samples were heat treated in a furnace and spectra were only taken before and after heat treatment; that prohibits a direct comparing to measurements at a microscope heating stage. The $z_{1/2}$-excitonic peaks were more strongly reduced with increasing annealing time. Samples with CuCl also exhibit a higher dependence on annealing time than CuBr microcrystals containing samples (see fig. 5).

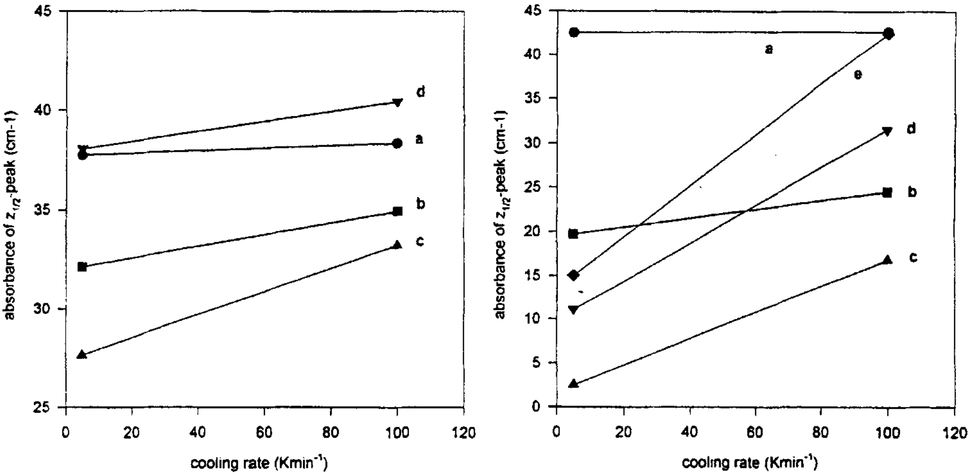

FIGURE 4: Absorbance of $z_{1/2}$-peak as function of cooling rate (measured at room temperature), t_{an} = 0.25 h, 4a: sample A 4b: sample B
a: 275 °C, b: 325 °C, c: 375 °C, d: 425 °C, e: 475 °C

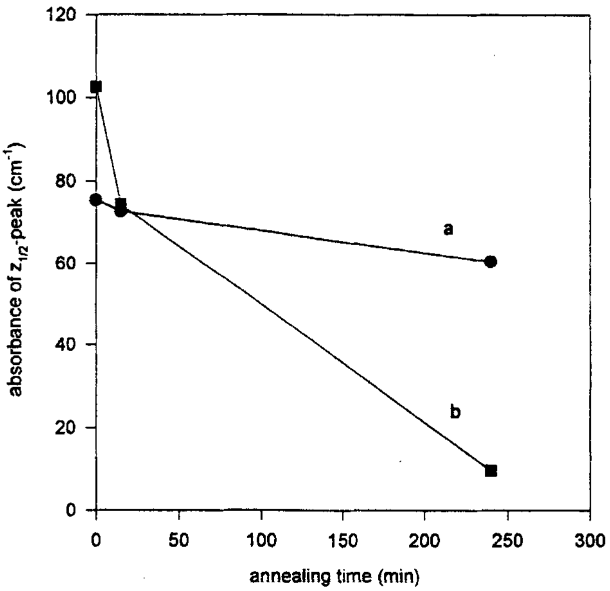

FIGURE 5: Absorbance of $z_{1/2}$-peak as function of time of the second annealing process (measured at room temperature) T_{an} = 325 oC, v_{cool} = 100 Kmin^{-1}
a: sample A b: sample B

INFLUENCE ON DARKENING

The curves of darkening vs. excitonic absorption after a second annealing exhibit a linear dependence over a wide range (see fig. 6). Only at small excitonic absorptions the curve shape differs from linear behaviour (corresponding to the highest temperature of the second annealing process: 425 °C). Figure 7 presents the spectra of difference by irradiation of the samples. An increasing of annealing time (e: 325oC/4 h) or a smaller cooling rate (f) cause a very pronounced decrease of darkening.

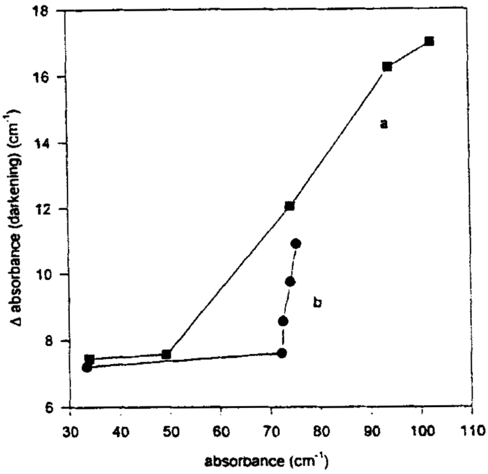

FIGURE 6: Darkening as function of absorbance of $z_{1/2}$-peak after a second annealing, t_{an} = 0.25 h, v_{cool} = 100 Kmin^{-1}, a: sample B b: sample A

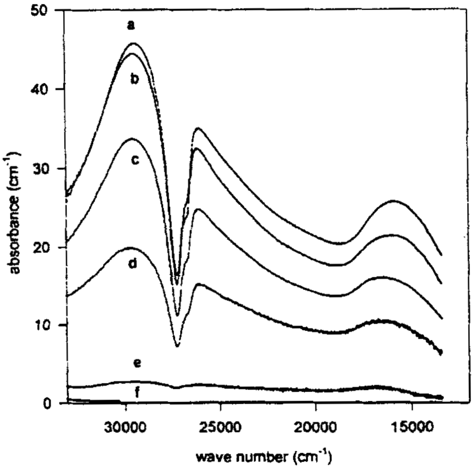

Figure 7: Spectra of difference by irradiation of sample B
a: without second annealing, b: second annealing: 275 °C/0.25 h, v_{cool}= 100 Kmin-1,
c: 325 °C/0.25 h, v_{cool} = 100 Kmin^{-1}, d: 375 °C/0.25 h, v_{cool} = 100 Kmin^{-1},
e: 325 °C/4 h, v_{cool} = 100 Kmin^{-1}, f: 325 °C/0.25 h, v_{cool} = 5 Kmin^{-1}

XRD MEASUREMENTS

CuCl microcrystals containing samples without a second annealing exhibit marked reflexes of cubic CuCl (low temperature modification LT) whereas one small reflex (100) of hexagonal (high temperature modification HT) CuCl is also observable. After a second annealing at 375 °C for 0.25 h and fast cooling also one reflex of HT CuCl crystals is found and the size of cubic CuCl crystals seems to be reduced. A slow cooling after heat treatment at 325 °C/0.25 h leads to a reduced size of cubic CuCl and an increase in HT CuCl intensity. If the samples were annealed at 325 °C for 4 h (including fast cooling), it has similar consequences on size of cubic CuCl and on appearance of hexagonal CuCl reflexes, but the effect of lower cooling rate is stronger. Measurements of CuBr containing glasses lead to a similar behaviour: with increasing of second annealing temperature, second annealing time or decreasing of cooling rate reflexes of γ-CuBr (LT) disappear (at room temperature XRD measures). The crystals were partly transformated into β-CuBr (HT) (see figure 8).

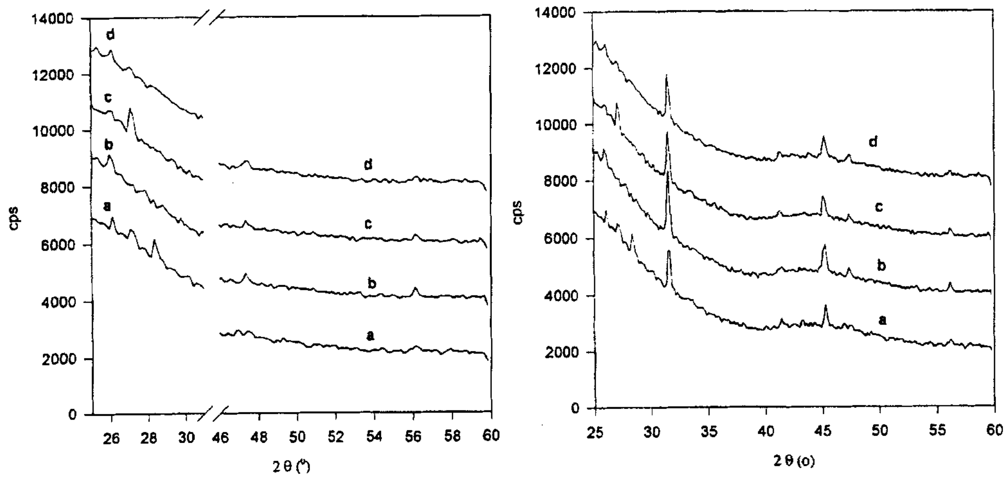

FIGURE 8: X-ray diffraction pattern (2 Θ = 21...35 ° and 46...60 °)
8a: sample B 8b: sample A
a: without a second annealing, b: second annealing: 325 °C/0.25 h, v_{cool} = 5 Kmin^{-1}
c: 325 °C/4 h, v_{cool} = 100 Kmin^{-1}, d: 375 °C/0.25 h, v_{cool} = 100 Kmin^{-1}

DISCUSSION

At a second annealing of photochromic glasses a decrease of darkening behaviour is to be observed, which directly correlates to a spectroscopical proved decrease of microcrystals. To decrease this excitonic absorbance it is not sufficient, to heat the samples up to the certain temperature and cool it down again. The process needs time: either by holding temperature for a time or by a slow cooling to room temperature. An increase in holding time or decrease of cooling rate raises the effect of decreasing of excitons absorbance. Above a maximum temperature of second annealing this effect falls again.

XRD investigations demonstrate a partly transition of the LT modification into the HT modification by the second annealing procedure. This transition from zincblende-structure-type into wurtzite-type is a reconstructional one, that means, bonds have to be broken for forming new bonds. Because of the high activation energy of this process, this transition is very slow, e. g., shows a high dependence on time. The hexagonal crystals or crystal regions do not contribute to the absorbance of excitonic peaks and to photochromism. This would sufficiently explain the results of the second annealing.

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