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NOTATION

- C_0 = initial concentration (microorganism's/litre)
 C_n = concentration after n passes through cavitation field
 e = kill efficiency
 n = number of times sample passed through cavitation field
 V = volume of cavitation field
 X = holding tank volume

$$\frac{C_n}{C_0} = \left[\frac{X - e \times V}{X} \right]^n \quad (3)$$

When this equation is applied to the yeast test data obtained, the resulting kill efficiency is 0.49. When it is applied to the test results for *Pseudomonas aeruginosa* in diesel fuel, the resulting kill efficiency is 0.45. These results were based on an exposure time of 3.15 seconds in the cavitation field.

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PHOTOCROMIC AND PHOTO-THERMO-REFRACTIVE GLASSES

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INTRODUCTION

Inorganic glasses are the main transparent material, which people have long used for observation (windows in buildings, windshields in cars, eyeglasses, prisms and lenses in optical instruments), light delivery (light bulbs, projectors, lasers, optical fibers), and fine arts (crockery, bijouterie, jewelry). The ability of glasses to change coloration after exposure to sunshine was well known since the last century. A new era in glass application was started

in 1949 by S.D. Stookey's publication (12) in which recording a permanent photographic image in silicate glass was described. This two-step process of exposure to UV radiation and thermal development that resulted in a crystalline phase precipitation in the exposed areas was similar to the classical photographic process. As a result of intensive research during a long period of time, a great number of different photosensitive glasses were developed, which have found very wide application in different branches of industry and personal use. When exposed to optical radiation, these glasses (and glass ceramics) change their optical properties (absorption, refraction, or scattering) instantly or after thermal development, permanently or transiently. Among the great variety of photosensitive glasses, we emphasize only the two most widely used types.

The largest commercial application was obtained for so-called "photochromic glasses," which exhibit reversible coloration after exposure to UV or visible light and can vary their absorption depending on the illumination level. Glasses that contained small concentrations of microcrystals of silver and copper halides, proposed by Armistead and Stookey in 1965 became the most widely used for reversible coloration (13). A peculiarity of these materials is that they are produced by glassmaking technology whereas the photochromic processes occur in microcrystals distributed in the glass matrix. Several hundred original papers were dedicated to different aspects of heterogeneous photochromic glasses in those years. The vast bibliography and detailed descriptions of these heterogeneous photochromic glasses were collected in books (3,4), and therefore we will not include a list of original publications in this article.

Another type of photosensitive glass, which is beginning its application in optics and photonics right now, is "photo-thermorefractive (PTR)" glass. If this glass is exposed to UV radiation followed by heat treatment, it varies in refractive index. A phase hologram in the volume of this glass was recorded in 1990 by Glebov and coauthors (5). The feature of this process is that homogeneous glass is exposed to light and a microcrystalline phase is produced in the volume of the glass matrix by a thermodevelopment process. No books have been written on this subject. The main results concerning phase hologram recording in glasses can be found in a few original papers (5-7) and a survey (8). Similar processes of photoionization followed by thermoinduced crystallization were studied for single- and full-color photography in polychromatic glasses, as described in (1, 9-12). Thus, these references can also be used for learning the basic physical phenomena that result from irradiation and development of PTR glasses. Some basic data concerning intrinsic absorption, electronic excitation, and nonlinear photoionization in multicomponent glasses can be found in (13,14).

PHYSICAL PRINCIPLES OF PHOTSENSITIVITY IN GLASSES

Photosensitivity is the variation in glass properties from exposure to optical radiation. Photoinduced processes can be caused by the absorption of light and consequent

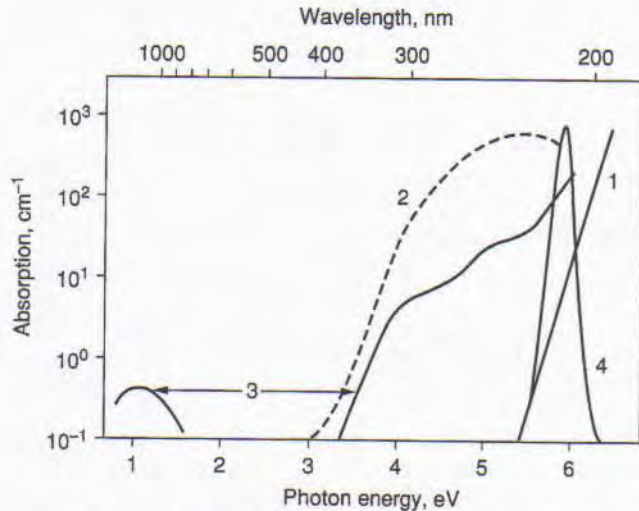


Figure 1. Absorption spectra of $25\text{Na}_2\text{O}-75\text{SiO}_2$ glass. 1: intrinsic absorption; 2 and 3: extrinsic absorption of 0.1 wt.% of Fe^{3+} and Fe^{2+} , respectively; and 4: color center generation spectrum (arbitrary units).

excitation of electrons from ground to upper levels by which these electrons can be delivered to other places (we will not consider heating and posterior melting or ablation). Absorption spectra of solids may be conventionally divided into three groups. Absorption due to electron transitions in defect-free substances of stoichiometric composition is called "intrinsic," "basic," or "fundamental" absorption. The absorption in atoms or molecules that are present as small additives is called "extrinsic," or "dopant," or "impurity" absorption. The absorption by defects in the host substance created by chemical or physical effects is called "induced," or "additional," or "defect" absorption.

The absorption spectra of widespread alkali silicate glass, which is the basis of the majority of technical glasses, are presented in Fig. 1. Intrinsic absorption (curve 1) is in the range of 210 nm (6 eV) and exhibits an exponential dependence of the absorption coefficient on photon energy (or wave number). This absorption is caused by basic structural units of silicate glass (Si-O-Na), which are called L centers. An example of extrinsic absorption in $25\text{Na}_2\text{O}-75\text{SiO}_2$ glass is shown by curves 2 and 3 for ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions, which determine the actual absorption of commercial silicate glasses in the near IR, visible, and near UV spectral regions. Induced absorption produced by UV and γ radiation (Fig. 2) is caused by ionization in the glass matrix and further trapping of electrons and holes at different glass matrix defects. The presence of different dopants and impurities results additional induced absorption bands. Extrinsic absorption can be caused by additional ions distributed in the glass matrix and also by bigger units, for example, microcrystals. The absorption spectra of borosilicate glass doped with copper and chlorine, which has undergone heat treatment, are shown in Fig. 3. Instead of absorption of copper ions in the glass in the far UV region, a narrow absorption peak near 380 nm (3.25 eV) is seen in these spectra, which corresponds to excitons in CuCl crystals precipitated in the glass matrix as the result of heat treatment. Induced absorption can

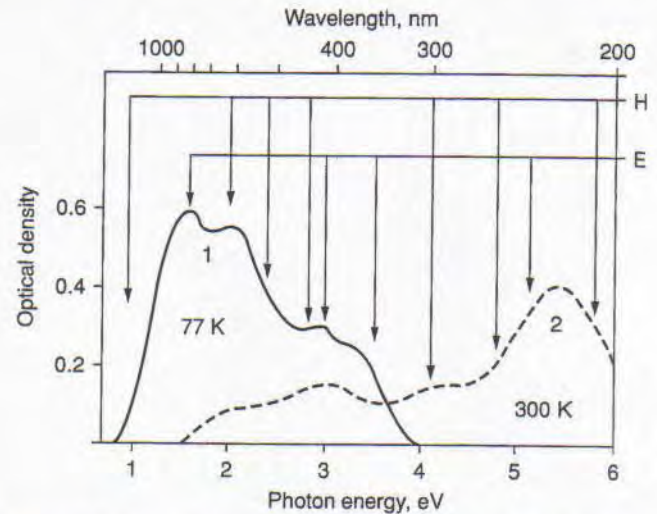


Figure 2. Induced absorption spectra of $25\text{Na}_2\text{O}-75\text{SiO}_2$ glass. 1: exposure to UV at 77 K; 2: γ irradiation at 300 K. Arrows show the positions of the absorption bands of electron (E) and hole (H) color centers.

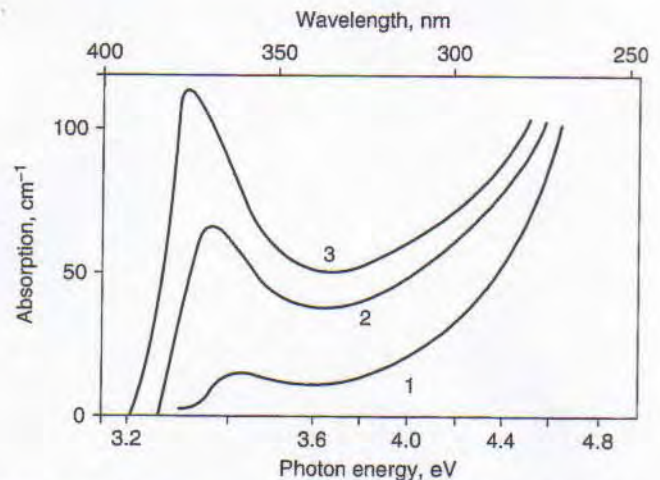


Figure 3. Absorption spectra of borosilicate glass doped with copper and chlorine after 2 hours of treatment at $T(^{\circ}\text{C})$: (1) 550, (2) 600, (3) 650.

also be produced by relatively big particles. Photoinduced precipitation of microcrystals of such metals as gold, silver, and copper causes additional absorption, usually called colloidal coloration.

Glass exposure to radiation whose photon energy is more than the intrinsic absorption edge (curve 1 in Fig. 1) causes photoionization in the glass matrix followed by the generation of both electron and hole color centers. The dependence of the induced absorption on the photon energy (or wavelength) is called the color center generation spectrum or the spectrum of photosensitivity (curve 4 in Fig. 1). Photoionization in the glass matrix (generation of both electron and hole centers) is impossible if the photon energy of the exciting radiation is less than a bandgap, which is determined by the position of the intrinsic absorption (curve 1 in Fig. 1). In other words, the long wavelength

edge of the color center generation spectrum (curve 4 in Fig. 1) coincides with the intrinsic absorption edge (curve 1 in Fig. 1).

The photosensitivity spectrum can be shifted to the long wavelength side if the glass is doped with some ions in a lower valence state, and the dopant's excited level is placed above the threshold of the charge carrier's mobility. In this case, a mobile electron can be trapped either by defect at an intrinsic electron center formation or by another dopant, that is, to recharge the activators. The depth of the dopant ground level in $\text{Na}_2\text{O}-3\text{SiO}_2$ glass is 5.2 eV for Fe^{2+} , 5.0 eV for Tb^{3+} , and 3.6 eV for Ce^{3+} . Comparison of these values with curve 3 in Fig. 1 shows that the ionization threshold of Fe^{2+} corresponds to the long wavelength edge of the absorption band whose maximum is at 6.5 eV (191 nm). Excitation using smaller photon energy causes tunnel ionization whose efficiency is about one to two orders of magnitude less than that of over-barrier ionization. The thresholds of tunnel ionization of dopants in $\text{Na}_2\text{O}-3\text{SiO}_2$ glass are 3.5 eV for Fe^{2+} , 3.1 eV for Tb^{3+} , and 3.1 eV for Ce^{3+} . Referring Fig. 1, one can see that the tunnel ionization of Fe^{2+} is obtained at an excitation of the long wavelength bands whose peaks are at 5.1 and 4.4 eV (243 and 282 nm) up to 3.5 eV (350 nm). Unlike intrinsic ionization that inevitably produces electron and hole centers, the only hole center generated from the excitation of dopant absorption bands is the same (but oxidized) dopant ion. All newly created centers are electron centers (either intrinsic or extrinsic).

The other way to shift photosensitivity to the long wavelength side is to use nonlinear ionization produced by powerful optical irradiation. In silicate glass exposed to pulsed radiation whose photon energy is more than half of the bandgap ($h\nu > 3$ eV, $\lambda < 400$ nm) and whose irradiance is more than $1 \text{ MW}/\text{cm}^2$, both electron and hole color centers appear as a result of two-photon ionization in the glass matrix. The final concentration of color centers is determined by equilibrium between two-photon generation and single-photon bleaching of color centers.

INDUCED COLORATION OF REVERSIBLE PHOTOCROMIC GLASSES

Generally, the term photochromism may be treated as any variation of color induced by optical radiation, but usually people use a narrower definition, which excludes irreversible color changes. So, photochromism is a reversible variation in color (i.e., of the absorption spectrum or spectrum of attenuation) of a material under optical radiation that relaxes when exposure stops. Naturally, when experimental conditions are changed, for example, a temperature change, the magnitude of the photochromic effect can vary (even to complete disappearance). Therefore, we shall call a photochromic material one that, under specified operating conditions, becomes colored by optical radiation and restores its transparency after radiation ceases.

Relaxation of induced absorption after illumination ceases is usually caused by thermal fading of color centers, which are not stable at a given temperature. This is the most important feature of photochromic materials

because reversibility of the photochromic effect means the absence of any stable induced centers generated by illumination. A great number of electron and hole color centers in silicate glasses produced by UV radiation (Fig. 2) leads to fatigue because of the progressive accumulation of stable color centers. This is the reason that these glasses are not used as photochromic materials, although photochromism was discovered in cerium-doped, reduced silicate glasses. Glasses doped with microcrystals of silver and copper halides (Fig. 3) show complete reversibility of coloration at room temperature and therefore have the widest commercial application.

The main feature of photochromic glasses, variable optical density both observed during exposure and upon its cessation, has to be taken into account to determine characteristics such as integral and spectral sensitivity, darkening degree and rate, thermal fading, and optical bleaching rates. Let us define the main concepts required for photochromic material characterization. Light absorption (or, more exactly, light attenuation or losses, that is the sum of absorption and scattering) is characterized by the transmittance, $\tau = I_{tr}/I_0$ (where I_{tr} and I_0 are the intensities of transmitted and incident light, respectively), or the optical density, $D = -\log_{10} \tau$. The optical density of a sample before irradiation (original absorption, clear glass) is D_0 (Fig. 4). The optical density of the sample at the moment exposure ceases (induced absorption, dark glass) is D_{exp} . The optical density in t seconds of the thermal fading process (induced absorption, partially relaxed glass) is D_t . The spectral dependences of τ_0 and D_0 are the transmission or absorption spectra of clear glass. The spectral dependences of τ_{exp} and D_{exp} are the transmission or absorption spectra of dark glass. Glass has a gray color if the absorption (transmission) spectrum is flat in the visible region. A brown color means that the absorption in the blue region is greater than that in the red region.

The dependences of D_{exp} and D_t on the time of illumination or aging are the kinetics of coloration and relaxation, respectively (Fig. 4). D_{exp} increases when the exposure time increases and comes to the equilibrium level D_e

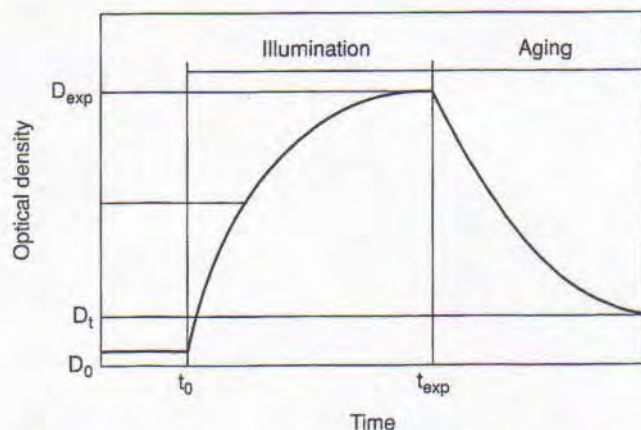


Figure 4. Kinetics of photochromic glass darkening under illumination and fading in the aging process. D_0 , D_{exp} , and D_t are the optical densities of clear, dark, and relaxed glass, respectively.

when the rate of color center generation is equal to the rate of thermal fading. The criterion of relaxation characterizes the degree of thermal fading in a certain time after illumination ceases:

$$K_{\text{rel}} = \frac{D_{\text{exp}} - D_t}{D_{\text{exp}} - D_0} \quad (1)$$

The value of that time interval should be selected on the basis of the practical applications of a photochromic glass. Thus, for photochromic lenses used as sunglasses, a time interval of 180 s is recommended. From Eq. (12), it is obvious that, if a glass has faded completely in that time, $K_{\text{rel}} = 1$. Contrariwise, if the induced absorption has not reduced at all in that time, $K_{\text{rel}} = 0$. Now, there are photochromic glasses whose K_{rel} vary in the entire range from zero to about one. K_{rel} for a particular glass can be changed by temperature variation.

An important parameter is the spectral sensitivity of a photochromic material, the dependence of the saturated photoinduced optical density (D_s) on the photon energy of the exciting radiation. This dependence is called the color center generation spectrum. The absorption edge of photochromic glass determines the position of the color center generation spectrum because photosensitive crystals absorb exactly in that region (compare curves 1 and 2 in Fig. 5). The short wavelength edge of the color center generation spectrum is connected with the decrease of the thickness of the layer containing color centers, that is due to the increase of the glass absorption coefficient. The long wavelength edge is caused by a decrease in the absorption and in the efficiency of photosensitive center ionization. These photosensitive centers are usually copper centers in silver halide crystals or excitons in a crystalline phase of copper chloride. Owing to that, the position of the maximum in the color center formation spectrum does not coincide with that of any maximum in the photochromic glass absorption spectrum. Moreover, its position is determined by the spectral shape of the photochromic glass absorption edge,

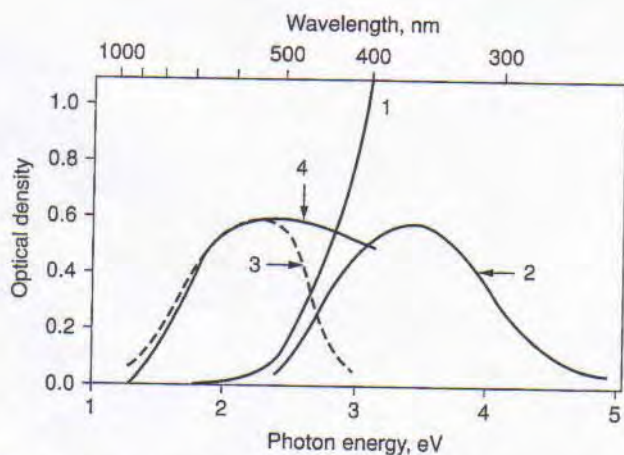


Figure 5. Spectra of glass doped with AgCl(Br). Absorption of original glass (12) and color centers (3), color center generation (13) and bleaching (4) efficiency. Sample thickness 5 mm.

is a function of the sample thickness, and drifts to the short wavelength side as the thickness decreases. The absorption spectrum of an exposed glass doped with AgCl microcrystals is presented in Fig. 5, curve 3. This absorption represents a wide band in the visible spectral range. The spectral shape of this band is usually ascribed to precipitation of colloidal silver particles on the surface of halide microcrystals. Curve 4 in Fig. 5 shows that excitation of the absorption band of color centers destroys these centers and causes optical bleaching. Thus, optical bleaching by visible light is a process additional to thermal fading, which accelerates the relaxation of darkened silver halide photochromic glass.

The photosensitivity of photochromic glasses doped with CuCl can be shifted from the UV region to the long wavelength side. Virgin photochromic glass is photosensitive only to UV irradiation and cannot be darkened by visible light. Excitation of glasses doped with CuCl that are exposed to UV radiation does not produce optical bleaching, as shown in Fig. 5 (curve 4) for silver halide glasses. On the contrary, initial additional absorption (induced by UV radiation) can be intensified by additional exposure to visible and even IR radiation having photon energy much below the ionization threshold of copper centers. Note that the power density of long wavelength irradiation must be high enough to produce this intensification. It is shown in Fig. 6 that the spectra of additional absorption produced in this glass after irradiation at various wavelengths are the same. Consequently, this long wavelength sensitivity results from generating new color centers by exciting the same color centers. Therefore this process is called "cooperative breeding of color centers."

The mechanism of two-photon cooperative breeding is as follows. Initial exposure to UV radiation causes ionization

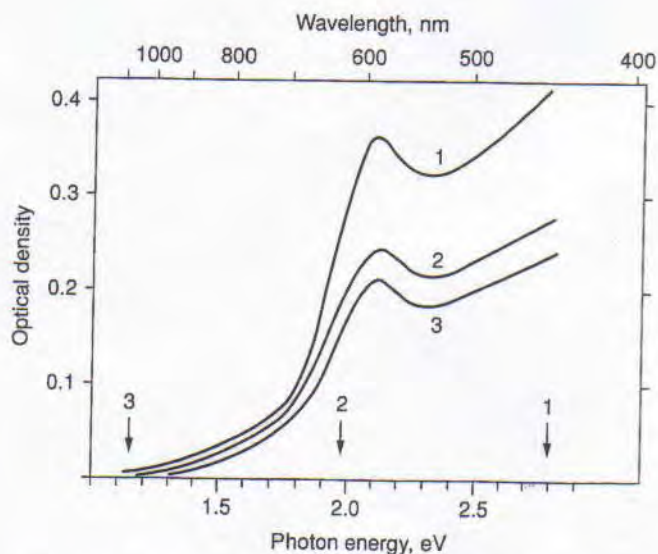


Figure 6. Spectra of induced absorption in copper halide photochromic glass (thickness 5 mm) after exposure to radiation at different wavelengths: (12) 440 nm (2.78 eV), (13) 633 nm (1.96 eV), and (3) 1060 nm (1.17 eV).

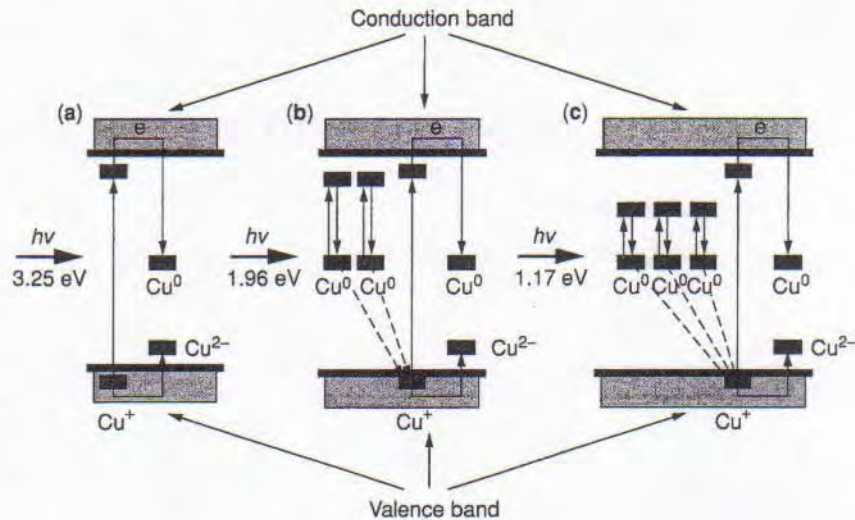


Figure 7. Energy diagram of the first stage of photochromic glass coloration at (a) short wavelength coloration, (b) two-photon cooperative breeding, and (c) three-photon cooperative breeding.

of a photosensitive center (Cu^+) and generates electrons and hole centers (Cu^{2+}). Then released electrons produce color centers by reducing copper (Cu^+) or silver (Ag^+) ions. The initial concentration of color centers (Fig. 7a) is determined by the number of UV-ionized photosensitive centers. This concentration can be rather small and even invisible to the naked eye. Linear absorption of two photons of visible light by two color centers causes a transition of these centers to excited states (Fig. 7b). Further, these centers simultaneously transfer the accumulated energy to the photosensitive centers (Cu^+) and return to their ground states. An excited photosensitive center releases an electron and converts to its ionized state in the same manner as after linear excitation, as illustrated in Fig. 7a. The released electron is trapped by an acceptor, converts to a reduced state (Cu^0), and this is a first stage in generating a new color center. Thus, the number of color centers increases after each cycle. This means that induced absorption increases in the process of exciting previously induced color centers without altering the spectrum of the induced absorption. The efficiency of this nonlinear process is proportional to the squared intensity of the exciting long wavelength radiation.

The coloration caused by exposure to pulsed IR radiation can be explained similarly to the three-photon cooperative breeding of color centers (Fig. 7c). The latter process obeys the cubical dependence of efficiency on the intensity of the exciting radiation. There are several important features of cooperative breeding of color centers. The first is a very high level of additional absorption because photosensitivity in this case is not connected with the sharp absorption edge of glass (Fig. 5) and a thick slab can be homogeneously colored. The second is the opportunity of localizing colored spots in arbitrary places of the bulk glass. The spots are produced by focusing the exciting beam because photosensitivity is proportional to the squared or cubical intensity of the exciting radiation and therefore, is concentrated near the focal plane. The third is an opportunity to store a latent image produced by UV radiation that can be revealed by photodevelopment.

HETEROGENEOUS PHOTOCROMIC GLASSES

Photochromic glasses co-doped with silver and copper halides are heterogeneous materials. They represent two-phase systems that consist of a vitreous host and dispersed photosensitive microcrystals. This is important because microcrystals show a reversible photochromic effect without fatigue. However, in a two-phase system, light attenuation is caused by absorption of each phase and also by scattering produced by the difference between the refractive indexes of the crystalline and vitreous components. Therefore, the parameters of the crystalline phase should be chosen to prevent strong scattering. The size of the particle of most photosensitive microcrystals, whose refractive index is about 2, should be no more than 10–20 nm to keep scattering below the level of acceptability for optical applications.

The main approach to producing dispersed microcrystals in a vitreous host is crystalline phase growth as a result of host glass heat treatment at temperatures from 500–700°C, depending on host composition. These temperatures correspond to a viscosity range from 10^{10} – 10^{13} poise. To secure crystalline phase precipitation, special requirements are applied to the host glass. First, this glass should be an oversaturated solution of the photosensitive phase (silver and copper halides) that allows effective diffusion of these components in the temperature range mentioned. Second, the solubility of the photosensitive components must drop quickly when cooling to allow the homogeneous glass to melt at high temperature and the crystalline phase to precipitate in the secondary heat treatment process. The last is usually connected with phase separation (immiscibility) and altered coordination of different components in the host glass.

The best glass, which satisfies the requirements mentioned before, is alkaline borosilicate glass. This glass matrix is the basis for almost all commercial photochromic glasses manufactured by a number of companies in different countries. Halides (Cl, Br, I) of silver and copper are photosensitive components, which are added to the batch.

Cations such as Mg, Ca, Ba, Zn, Cd, Al, and Pb, or anions such as P and S are used by different companies as additions to modify technical and end use properties. These compositional changes lead to variations in photosensitivity, the criterion of relaxation, and induced absorption spectra. Photochromic glasses can be divided into two large groups: silver halide glasses that have small concentrations of copper, which usually exhibit faster relaxation and lower sensitivity and copper halide glasses that have small concentration of silver, which exhibit slower relaxation and higher sensitivity. In silver halide glasses, small additions of copper are a sensitizer.

The traditional schedule for photosensitive phase creation, "bottom-to-top," consists of four stages: melting, rough annealing and cooling to room temperature, additional heat treatment (roasting), and final annealing. Final annealing is necessary for stress relaxation because crystalline phase precipitation occurs at temperatures above the glass transition temperature. The other method of sensitization is "top-to-bottom," which is used for mass production because of heat energy saving. In the latter, the glass casting cools down to roasting temperature but not to room temperature. It requires the other schedule (time and temperature) because the most effective growth of nucleation centers occurs at temperatures below the roasting temperature.

OPTICAL WAVEGUIDES IN PHOTOCHROMIC GLASSES

The largest commercial application of photochromic glasses is for sunglasses. Tens of millions of photochromic lenses are produced worldwide each year for this purpose. However, the alkaline borosilicate origin of photochromic glasses allows some other applications in modern optics and photonics. It is well known that these glasses are suitable for ion exchange and, consequently, planar and channel waveguides can be created on this glass. Besides that, the mildly sloping dependence of photochromic glass viscosity on temperature allows creating of optical fibers. The optical properties of photochromic waveguides compared with bulk photochromic glasses are unusual because of structural transformations in the ion-exchanged layers or in the drawn fibers and the peculiarities of light propagation in waveguides. An important feature of ion-exchanged glass is incompleteness of structural relaxation. The exchange of ions that have different radii creates stresses in glass. These stresses produce strong differences between the refractive indexes of waveguide modes that are orthogonally polarized (birefringence). Compression of silver halide photochromic glass after substituting Na^+ by K^+ at temperatures below the glass transition temperature reaches 1 GPa and produces birefringence up to 20% of the total refractive index variation, as shown in Fig. 8.

Exposure of waveguides in photochromic glasses to UV radiation produces reversible coloration. This means that ion-exchange treatment does not destroy the photosensitive crystalline phase and this technology is available for photosensitive waveguide fabrication. However, parameters of coloration and relaxation of photochromic waveguides are different compared to bulk glass. For silver

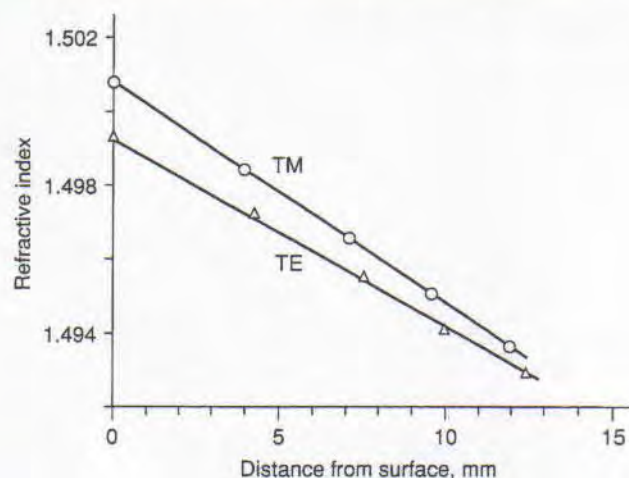


Figure 8. Refractive index profiles of photochromic glass after $\text{Na}_{\text{glass}}\text{-K}_{\text{melt}}$ ion exchange. TE or TM polarizations mean electric or magnetic field oriented along the surface, respectively.

halide glasses, the criterion of relaxation in waveguides is more than that in bulk glass. This means that relaxation in waveguides occurs faster. For copper halide glasses, relaxation in the waveguide was not detected, which means that the coloration of these waveguides is stable. There is a difference in photosensitivity between different waveguide modes. Modes with low numbers propagate near the surface and have lower sensitivity than modes that have a large number and propagate in deep layers. This difference is caused by copper (which is a sensitizer) depletion in the surface layer as result of copper exchange for potassium or other ions. This phenomenon can be used for mode selection.

The other feature of photochromic waveguides is anisotropy of photosensitivity and induced coloration. This phenomenon is connected with ion-exchange stresses. Dichroism (the difference between induced absorption for orthogonal polarizations) is proportional to birefringence in a waveguide. It is important to note that photosensitive microcrystals are plastic or melted at the temperatures of ion exchange. Therefore, dichroism is determined by stresses and also by orientation of liquid drops of the photosensitive phase caused by ion-exchange stresses.

The discrete structure of light propagation in photosensitive planar waveguides gives one more opportunity for multiplexing by mode selection. If a mode in such a waveguide (Mode #1 in Fig. 9) is excited by actinic radiation, the waveguide becomes colored. The spatial profile of induced absorption is determined by the spatial profile of the exciting modes intensity. As a result, a sort of distributed absorbing mask will be formed in the waveguide whose absorption profile is similar to that of the intensity distribution of actinic radiation in the waveguide. Consequently, losses for mode #1 increase after excitation of this mode by actinic radiation. The attenuation of other modes is determined by overlapping of their fields by the distributed mask, that is, by the field of the mode that induced this absorption. Because field profiles for the modes that have different numbers essentially differ from each other

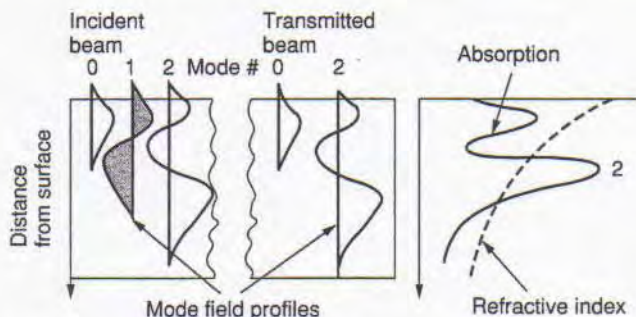


Figure 9. Sketch of a waveguide mode selector. The darkened profile corresponds to the exposed mode, which produces a similar profile of photoinduced absorption and prevents propagation of this mode.

(Fig. 9), the losses for different modes should be significantly different. An example of a mode spectrum of a planar waveguide excited by actinic radiation in the TE_0 mode is shown in Fig. 10. A mode selection of about 10 dB/cm can be reached without special effort in planar waveguides on commercial photochromic glasses. The problem of mask bleaching can be solved by using probe radiation at longer wavelengths, where bleaching is not effective, or using, as described earlier, cooperating breeding of color centers for writing by high-power radiation.

Optical fibers were drawn from photochromic glasses. It was found that thermal treatment of these fibers produces photochromic properties. Fiber plates were made from photochromic glass as a core and a transparent optical glass as a cladding, or vice versa. High contrast was obtained in this fiber element compared to bulk photochromic glass plate. This feature of photochromic fiber plate is determined by gradual leakage of actinic radiation from transparent glass to photochromic glass. This effect increases the length of the interaction of actinic radiation with photochromic glass and, consequently, increases dramatically the induced absorption and possible contrast of a photochromic attenuator.

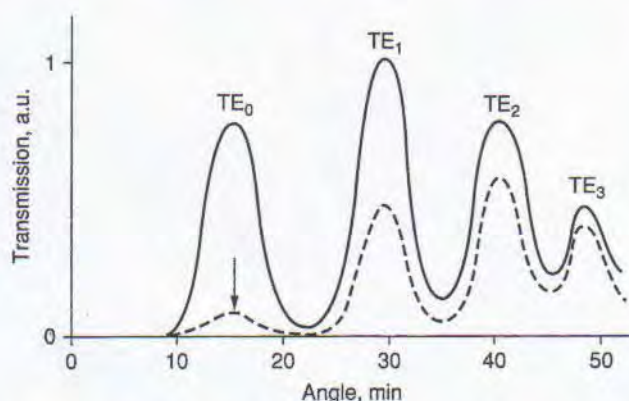


Figure 10. Effect of exposure to powerful excitation of the fundamental mode (shown by arrow) on the dependence of photochromic waveguide transmission on the angle of incidence onto the input coupler prism (spectrum of waveguide modes). Solid lines before exposure, dashed lines after exposure.

INDUCED REFRACTION THROUGH IRREVERSIBLE PHOTOINDUCED CRYSTALLIZATION

It is clear that photochromic glasses can be used for recording information. Actually some photos and holograms were recorded in these glasses but no great success was obtained because of small contrast in photography and small diffraction efficiency in holography. For highly efficient holography, it is necessary to produce variation in the refractive index but not in the absorption coefficient. The refractive index in glasses, where color centers are induced by radiation, can vary for very small values, less than 10^{-6} . This is not enough for efficient diffraction. Recent discovery of a strong photoinduced refractive index variation in Ge-doped silica opened a new very promising approach for efficient Bragg grating recording in optical fibers. Another approach, which allows an increase of sensitivity of several orders of magnitude compared to Ge-doped silica and avoids interaction between writing and diffracted beams, is based on a two-step process of exposure and development in multicomponent silicate glasses doped with fluorine, silver, and cerium.

Phase volume holograms of high diffraction efficiency were produced in lithium aluminum silicate and sodium zinc aluminum silicate glasses doped with silver and cerium by exposure to UV radiation followed by thermal treatment. Diffraction was caused by a difference in refractive indexes in exposed (enriched by microcrystals) and unexposed (original glass) areas. This phenomenon is called the "photo-thermorefractive" process. Glasses that possess these properties are called "photo-thermorefractive" (PTR) glasses. This two-step process (exposure and thermal development that leads to crystallization) was used earlier to record a translucent image in glass due to light scattering caused by a difference between the refractive indexes of the precipitated crystalline phase and the glass matrix. Later, colored images were recorded in similar glasses by photothermal precipitation of a number of complex crystals of different compositions, sizes, and shapes.

The sequence of processes, which occurs in these glasses and produces coloration, follows (Fig. 11). The first step is exposure of the glass to UV radiation, which ionizes a cerium ion. The electrons released from cerium are then trapped by a silver ion. As a result, silver is converted from a positive ion to a neutral atom. This second stage corresponds to latent image formation, and no significant changes in optical properties of glass occur, except light coloration in near UV and blue regions.

The next step in the process is obtained by thermal development at elevated temperatures. The high diffusion coefficient of silver atoms in silicate glasses leads to the creation of tiny silver crystals at temperatures from 450–500°C. A number of silver clusters arise in exposed regions of the glass after aging at these elevated temperatures. This is the third stage of the process. Further, these silver particles serve as the nucleation centers for sodium and fluorine ion precipitation. Cubic sodium fluoride crystal growth occurs at temperatures from 500–550°C because the PTR glass composition is an oversaturated solution of these components. This is the last step, which finishes the photo-thermorefractive process. Further heat treatment

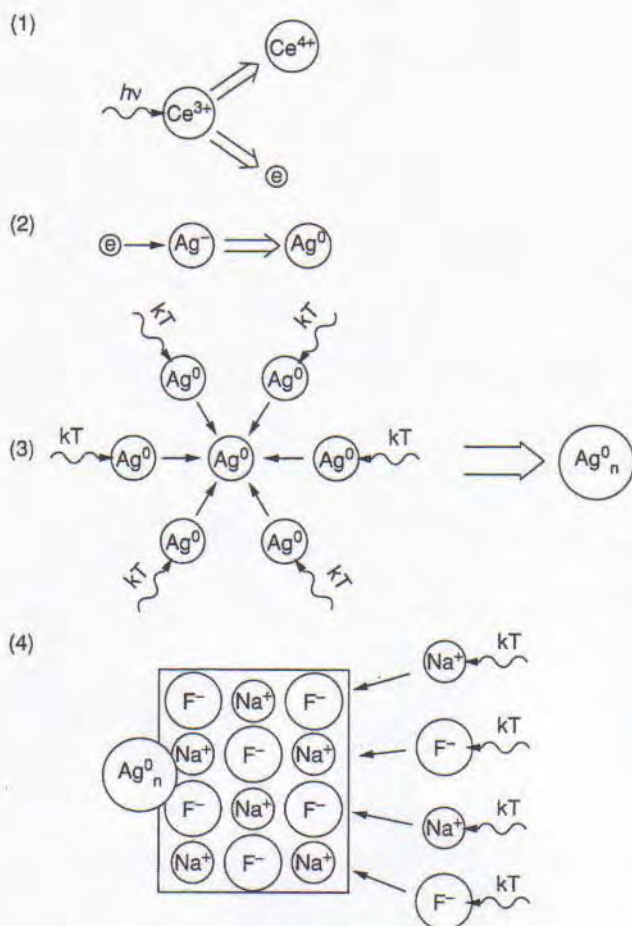


Figure 11. Stages of the photo-thermorefractive process.

leads to the growth of elongated pyramidal complex Na, Ag-F, Br crystals on the surface of cubic NaF crystals. This mixture of crystals can produce an opal coloration in large crystal sizes or a yellow coloration caused by colloidal silver precipitated on the interfaces of dielectric crystals. A second exposure to UV followed by a second heat treatment produces a different coloration because of metallic silver reduction on the surfaces of the dielectric pyramids. The final resulting coloration depends on the size and aspect ratio of these silver particles. These two last steps are used for photography because strong scattering does not allow using them in holography.

A refractive index decrease of about 5×10^{-4} occurs in the areas of glasses exposed to nitrogen laser radiation at 337 nm. The refractive index of NaF in the red spectral region is $n_{NaF} = 1.32$ compared to the refractive index of PTR glass $n_{PTR} = 1.49$. The small value of the refractive index change is due to the small volume fraction of the precipitated crystalline phase, which produces no scattering in the exposed volume. However, it is sufficient to result in highly efficient Bragg grating recording in samples more than several hundreds of microns thick. This photo-thermoinduced refraction is stable up to 400°C. The photosensitivity is in the range of several tens of mJ/cm^2 at wavelengths in the absorption band region of Ce^{3+} , which has a maximum

near 300 nm and a long wavelength tail up to 400 nm. This means that several commercial lasers such as N_2 , Ar, and He-Cd, can be used for recording. Once developed, holograms in PTR glass are not destroyed by further exposure to visible or UV radiation.

PHOTO-THERMOREFRACTIVE GLASS

The composition (mol. %) of PTR glass which was used for hologram recording is $15Na_2O-5ZnO-4Al_2O_3-70SiO_2-5NaF-1KBr-0.01Ag_2O-0.01CeO_2$. Absorption spectra of PTR glasses are presented in Fig. 12. Figure 12a shows the UV part of the absorption spectrum. One can see the wide absorption band of Ce^{3+} that has a maximum at 305 nm. The short wavelength absorption in the region $\lambda < 270$ nm is due to several components, such as Ce^{4+} , Ag^+ , Br^- , and Fe^{3+} . The short wavelength edge, at which writing radiation is attenuated by two times in the recording medium (optical density about 0.3), is placed at 330 nm for a 1-cm thick plate and at 265 nm for a 1-mm thick plate. The range of photosensitivity of this glass is from 280–360 nm.

Absorption of PTR glass is less than 0.01 cm^{-1} in the visible and near IR regions, which is close to the limit of measurements, and therefore it is not shown in Fig. 12. One can see in Fig. 12b that detectable absorption occurs at wavelengths higher than 2700 nm. Absorption in this spectral region is usually ascribed to different vibrations of hydroxyl groups in the glass network and reaches several cm^{-1} in regular silicate glasses. Hydroxyl absorption in fluorine-containing PTR glass is lower compared to similar fluorine-free silicate glass. This phenomenon is caused by high volatilization of HF molecules, which can result from the interaction of fluorine and hydrogen in the glass melting process. This decrease of IR absorption in PTR glass results in an opportunity for PTR use in the middle IR region up to 4300 nm for 1-mm thick specimens.

Additional absorption of PTR glass under UV exposure that is used in hologram recording in this glass is shown in Fig. 12c, curve 1. Detectable photoinduced absorption is seen only in the UV region. Even at the recording wavelength, this absorption is less 0.1 cm^{-1} and cannot impact the recording process significantly. The small tail of the induced absorption spectrum in the blue region can be distinguished by the naked eye as a slight yellow coloration of the exposed area. Thermodevelopment causes colloidal silver and sodium fluoride precipitation in the glass matrix. Fluoride crystals are colorless and can result in scattering if the size of the crystals is too large (more than 100 nm). A shoulder near 450 nm in the additional absorption spectrum after thermal treatment in Fig. 12c (curve 2) is ascribed to silver particles in glass matrix. One can see that the visible additional absorption does not exceed 0.3 cm^{-1} and 0.03 cm^{-1} in the blue and red regions, respectively. This means that losses in this region do not exceed a few percent for a 1-mm thick plate. Additional absorption in the whole IR region is not detectable and therefore is not shown in Fig. 12c. Consequently, this glass can be used successfully at all wavelengths important for lasers and optical communication in the visible and near IR regions.

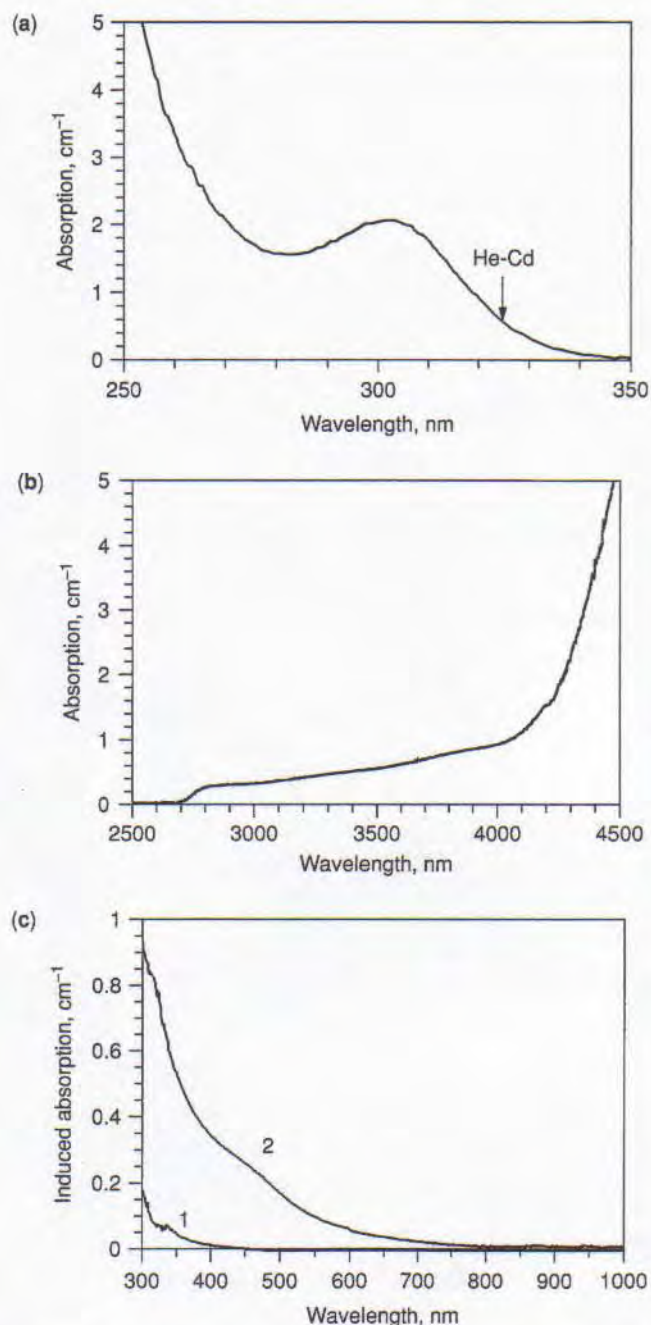


Figure 12. Absorption spectra of PTR glass: (a) and (b) original glass in the UV and IR spectral regions, (c) induced absorption after exposure to 325 nm for 400 mJ/cm² (12) and consequent thermal development for 1 hour at 520°C (13). Arrow shows the position of the wavelength of the writing He-Cd laser.

Optical microscopy of exposed and developed samples used for induced absorption measurements has shown optical inhomogeneities in the exposed region. The structure of these inhomogeneities appears as a series of parallel, continuous, aligned filaments whose widths are tens of microns oriented in the direction of light propagation in the glass sample. These microscopic features are caused by structures whose different refractive indexes arise in glass

processing (phase structures). It is proved that these phase patterns are not an intrinsic feature of PTR glass but are caused by various defects of the sample bulk and surfaces. Some additional patterns were found in micrographs; they are combinations of different rings and fringes. It was found that they are recordings of the interference patterns produced by matching propagating beams to beams consequently reflected from the back and front surfaces of different elements in the optical setup. Diffraction of the exciting beam on different apertures produces systems of straight or curved fringes that have variable periods dependent on the shape and position of the aperture. It is necessary to make special adjustments to eliminate these interference and diffraction patterns in the plane of the recording to avoid these parasitic structures. Therefore, the homogeneity of the photosensitive medium (including surface and volume defects) and the writing beam (including interference and diffraction patterns of low visibility) must be tested to avoid undesirable losses.

The pattern of probe radiation transmitted through exposed area consists of the zero and first orders of diffraction but exhibit some rings. The diameters and positions of these rings on the screen depend on the incident angle of the probe beam and on the feature of the writing pattern. The origin of these rings follows. Each medium causes scattering of propagating light. Therefore, even for single beams propagating in a photosensitive medium, one can observe an interference pattern produced by matching the original and scattered beams. In this case, the probe beam used for hologram reading should be scattered twice. The first time is regular scattering by the medium. The second time is scattering produced by a hologram of scattered light recorded together with the main hologram. This hologram can be completely reconstructed only by the reading beam of the same wavelength and direction as the writing beam. When the wavelengths or the directions of the writing and reading beams are different, the whole hologram of scattered light cannot be read out because its wavefronts are not planar. At each angle of incidence, the reading beam can read only that part of the hologram, for which Bragg conditions are satisfied. Because the angular diagram of scattering has cylindrical symmetry, this part should be a ring. All phase defects mentioned (filaments, fringes, and rings) appear in all materials but they are visible well in PTR glass because of the high homogeneity and transparency of this material.

BRAGG GRATINGS IN PTR GLASS

The dependence of the absolute diffraction efficiency of Bragg gratings recorded in PTR glasses in the thermal treatment period is shown in Fig. 13. The specimen exposed for 400 mJ/cm² has undergone consecutive thermal treatments for 10–15 minutes each at 520°C and in intervals between, was cooled down to room temperature for diffractive efficiency measurements. The absolute diffraction efficiency is

$$\eta_A = \frac{I_1}{(1 - \rho)^2 I_L} \quad (2)$$

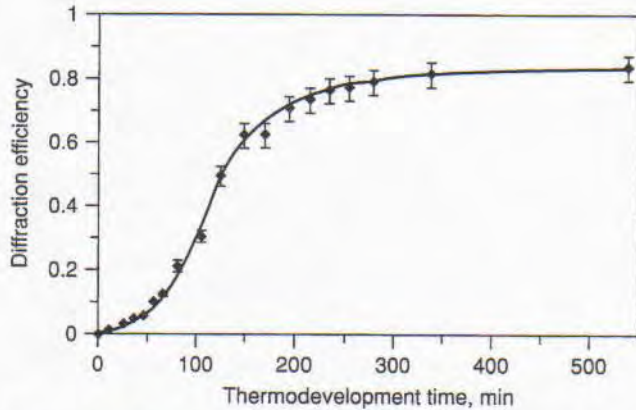


Figure 13. Effect of the period of thermal treatment on the absolute diffraction efficiency of a Bragg grating in PTR glass. Exposure 400 mJ/cm^2 at 325 nm , spatial frequency 600 mm^{-1} . Development at 520°C . Specimen thickness 1.42 mm .

where I_L and I_1 are the intensities of the incident and diffracted beams, respectively. The reflection coefficient (ρ) is calculated by the Fresnel formula $\rho = (n - 1/n + 1)^2$.

The dependence of diffraction efficiency versus development time has an inflection point at the beginning of the process and is saturated at the 85% level after long heat treatment. Note that this multiple heat treatment is not the same as a regular development for one or several hours because this procedure includes multiple heating and cooling. However, the curve in Fig. 13 shows a tendency for the diffraction efficiency to approach a high value after some exposure at elevated temperature.

The growth of diffraction efficiency in increasing periods of thermal development is obviously caused by refractive index changes that result from crystalline phase precipitation. Figure 14 shows the dependence of the refractive index on the thermal treatment period. This photothermoinduced refractive index was calculated from

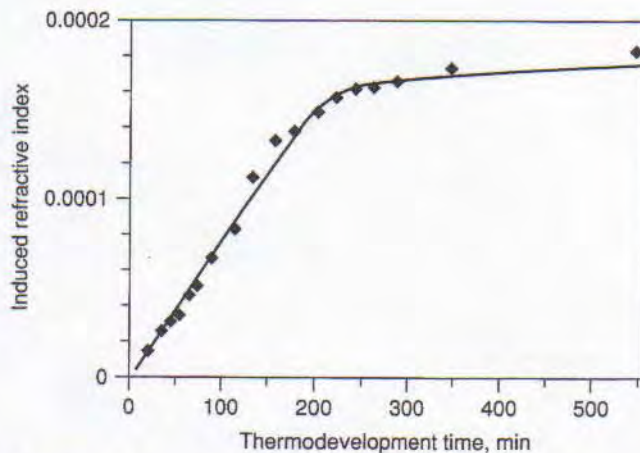


Figure 14. Effect of the period of thermal treatment on the induced refractive index. Exposure 400 mJ/cm^2 at 325 nm , spatial frequency 600 mm^{-1} . Development at 520°C . Specimen thickness 1.42 mm .

Kogelnik's equation:

$$\delta n = \frac{\lambda \cos \Theta \arcsin(\sqrt{\eta_R})}{\pi d}, \quad (3)$$

where λ is the wavelength of the reading beam, Θ is the Bragg angle, and d is the thickness of the specimen. The linear dependence of induced refractive index on the thermal treatment period is present in Fig. 14. The function $\delta n(t)$ shows no inflection point compared to $DE(t)$ (Fig. 13). The linear dependence of $\delta n(t)$ up to the value of 0.00015 allows writing high efficiency holograms in glass plates more than several hundreds of microns thick. The optical quality of inorganic glass allows using plates up to several centimeters thick. The saturation of the diffraction efficiency in Fig. 13 corresponds to the refractive index saturation at about 0.00017 in Fig. 14. No oscillations of diffraction efficiency were recorded in this experiment in long development periods up to 13 hours. This means that no significant result exceeding π for the induced phase was obtained and, consequently, no additional refractive index growth occurred.

The effect of the spatial frequency of the interference pattern on the diffraction efficiency of the grating in PTR glasses is shown in Fig. 15. This was measured in a thin sample of 1.65 mm in a transmittance configuration when writing (325 nm) and reading (633 nm) beams were directed from the same side of the glass plate. This configuration allows spatial frequency variations below 2500 mm^{-1} . Exposure or development of gratings was not optimized for different spatial frequencies. No significant dependence of diffraction efficiency on special frequency can be observed in the region from $300\text{--}2500 \text{ mm}^{-1}$ in Fig. 15. The absence of a drop in the frequency response at low frequencies is a feature of the PTR process, which requires transport of species in the glass matrix to build single crystals (tens of nanometers) and does not require transport of species between exposed and unexposed areas, as is necessary in photorefractive crystals. The

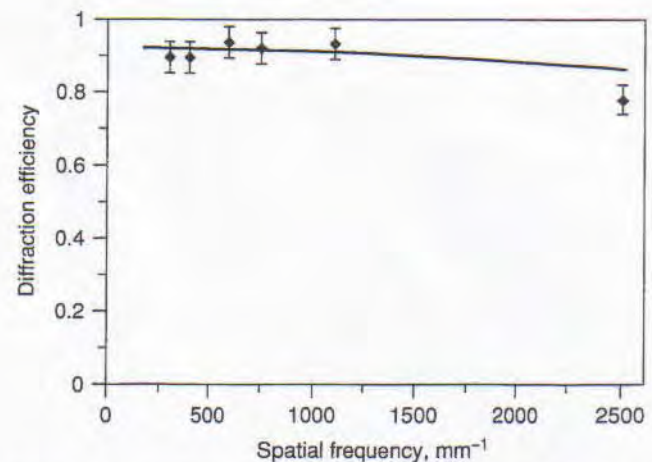


Figure 15. Dependence of the absolute diffraction efficiency on the spatial frequency of the grating. Exposure 600 mJ/cm^2 at 325 nm , development 90 min . at 520°C . Specimen thickness 1.65 mm .

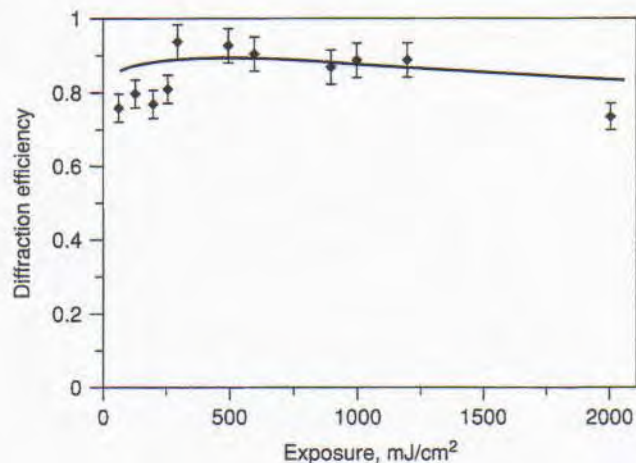


Figure 16. Maximum absolute diffraction efficiencies of Bragg gratings in PTR glasses for different exposures to the radiation of a He-Cd laser at 325 nm.

absence of a drop at high spatial frequencies means that no fringe smearing occurs in the developed interferogram and, consequently, no detectable diffusion of components at distances comparable with the half-period of the gratings studied (up to 200 nm) occurs in PTR glass during thermal processing. These data show that diffusion of glass components in the development process cannot affect the saturation in Fig. 14, which was observed for gratings that have a spatial period of 1600 nm. The lack of drop in the amplitude-frequency response at low frequencies (Fig. 15) is an advantage of PTR glasses compared to photorefractive crystals; this results in a distinct opportunity to design holographic optical elements that have very small diffraction angles.

An interesting consequence of the low level of induced losses (Fig. 12c, curve 2) is the rather low sensitivity of PTR-grating diffraction efficiency on exposure because underexposure can be compensated for by overdevelopment, and vice versa. Figure 16 illustrates this feature of PTR glass. In this figure, the best diffraction efficiencies for specimens of different thickness from different melts, which had undergone different development procedures, are plotted versus exposure to the radiation of a He-Cd laser. A high absolute diffraction efficiency of 80% and more is observed in Fig. 16 for exposures that ranged between 50 mJ/cm² and 5 J/cm².

SUMMARY

Photochromic glasses that have completely reversible coloration are made of borosilicate glasses doped with microcrystals of copper and silver halides. These glasses are sensitive to near UV radiation. Photosensitivity can be extended to visible and near IR regions by cooperative breeding of color centers. Induced coloration is a wide band that covers the whole visible region. Photocontrolled waveguides can be fabricated in photochromic glasses. These waveguides can serve as attenuators and mode selectors. Photo-thermorefractive glasses that have irreversible

photoinduced refraction are aluminosilicate glasses doped with silver, cerium, and fluorine. These glasses are sensitive to near UV radiation. Their photosensitivity is comparable with the best organic and inorganic materials, it allows wide variations of exposure because of image amplification in the thermal development process, and it has high diffraction efficiency and high transparency from the UV to the IR region.

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PIEZOELECTRICITY IN POLYMERS

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INTRODUCTION

The diverse group of "smart" piezoelectric materials is distinguished by their ability to react actively to changing stimuli as a result of converting mechanical to electrical energy and vice versa. Synthetic piezoelectric polymers, an integral part of the "smart" materials group, exhibit a type of behavior that is often compared with biological reactions involving transformations of the sensed information into the desired response. Due to such