Phototropic Glasses

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Phototropism

Phototropism was discovered by Marckwald in 1899. He noticed that certain crystalline substances discolored under the influence of light, reverting once again to their original state in the dark. More generally nowadays, the term phototropism is used to describe a reversible change between two states of different optical absorption due to the action of electromagnetic radiation (Fig. 1). Photochromism is a special case of this in which at least one of the states absorbs light in the visible region of the spectrum.

Phototropism obeys the Grotthus-Draper Law of photochemistry, that only light actually absorbed by the material can have an effect. When a phototropic medium is irradiated, a dynamic equilibrium is set up between the forward and back reactions; the system itself is fully reversible (*1*).

$$\text{colorless} \underset{\text{decrease in light intensity}}{\overset{\text{increase}}{\rightleftharpoons}} \text{colored}$$

The first description of the reversible darkening of silver halide crystals on irradiation with visible light was given by R. W. Pohl at the end of the 1930's (*2*). More recent investigations have been extended to the interaction of γ-rays with As-Mn-doped borate glasses (*3*).

Many inorganic substances show phototropic behavior in the solid state, some even in solution (*4*). Take, for example, a crystal of the mineral sodalite ($Na_8[Al_6Si_6O_{24}]Cl_2$). Under the influence of X-rays it changes from colorless to blue, but returns to the original state on heating to 450°C.

Phototropic and *photosensitive* glasses should not be confused. Color changes in the latter occur irreversibly.

Phototropism in borosilicate glasses with silver halides as the active components was first reported by Stookey and Armistead (*5*). These authors describe a phototropic glass they had produced by fusing together a mixture of silver salts and halides with a quantity of glass at 1250–1450°C followed by annealing. Other workers have implanted silver into the glass surface by ion exchange (*6*).

Figure 2, taken from the excellent review by G. Gliemeroth and K.-H. Mader, shows the most important features of phototropism. On exposure to light, the optical transmission falls rather steeply to a constant value (the saturation transmission), i.e., the extinction (optical density) increases. When the light source is removed the system returns to the starting value of approximately 90% transmission after a few minutes.

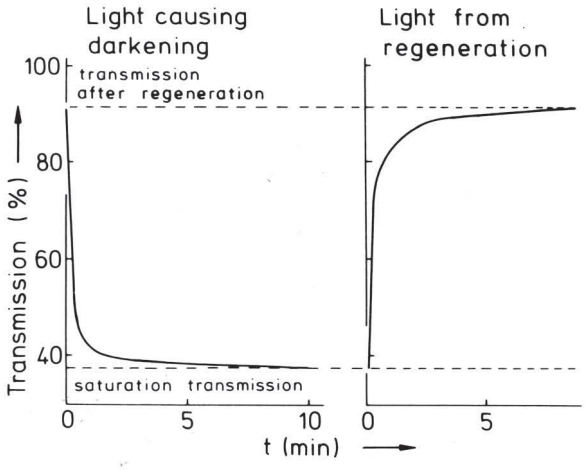

Figure 2. Darkening and regeneration of a silver halide-containing phototropic glass at 545 nm. Glass no. 3 from table. Left: transmission reduction during stimulation with Xe light (8000 lux); Right: variation of transmission after light source removed. (T = 20°C, sample thickness = 2 mm). From (*1*).

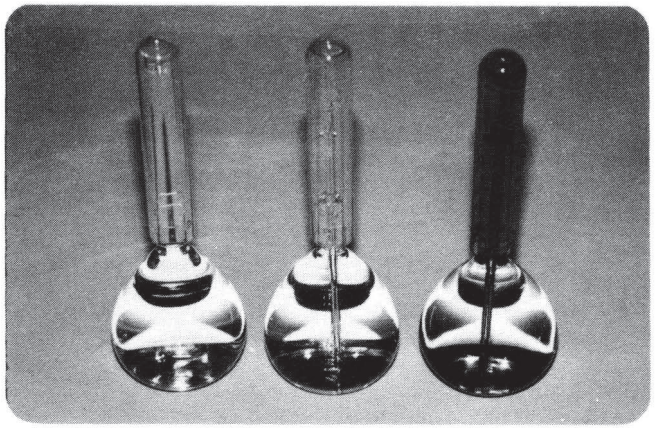

Figure 1. Vessels irradiated in neutron activation analysis experiment at the Garching research reactor (FRM). Left: quartz (10^9 rad). Middle: suprasil (10^9 rad, slight blue γ-induced luminescence). Right: suprasil unexposed. At 200°C thermal bleaching of the irradiated quartz can be accomplished within a few minutes.

Composition of Typical Industrial Phototropic Glasses in Weight Percent [a]

Ingredient	1	2	3
SiO_2	54.0	0.8	...
B_2O_3	16.0	46.5	55.0
Al_2O_3	9.1	22.3	8.0
Na_2O	3.0	3.5	...
K_2O	1.4	1.6	...
Li_2O	2.3	...	0.3
PbO	4.3	0.2	29.6
ZrO_2	1.9	2.2	...
BaO	6.6	1.7	2.0
MgO	...	7.7	2.0
P_4O_{10}	...	0.3	...
Ag_2O	0.27	0.26	0.55
Cl	0.5	2.6	0.4
Br	0.5	2.3	0.7
F	0.1	8.8	1.4
CuO	0.03	0.04	0.03
	100.00	100.80	99.98

[a] From ref. (*1*). The data are based on chemical analysis (composition optimized by usual materials tailoring methods).

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Structure and Manufacture of Phototropic Glasses

The table shows the composition of some silver-halide-based phototropic glasses. Gliemeroth and Mader stress in their review (*1*) that so many glass/silver halide combinations are known today to be phototropic that it is difficult to find examples, made by fusing the components together, that do not show this property.

(Note that the glasses in the table contain considerably more halide than silver. The excess halide is bound to other metals present, replacing some of the oxygen in order to preserve the cation/anion charge balance.)

The choice of the basic matrix glass type depends on the particular requirements for the product: refractive index, mechanical properties, chemical stability, etc., whereas the active, phototropic component is always a silver halide AgX (X = Cl, Br). The glass matrix can be compared to a solvent for particles, which contain silver halide.

The role of the fluoride which does not directly take part in the phototropic reaction is not yet completely understood, but it seems to facilitate the reversibility of the process (note that no AgF is present in photographic emulsions).

After annealing, these are present as a separate phase with a concentration of the order of 10^{15} particles/ml, have a mean diameter of 100 Å and are separated by distances of around 600 Å. The size of the precipitates varies with the temperature program used in the manufacture. Electron micrographs of transparent phototropic glasses can be used to investigate the particle-size distribution. Particles with diameters between 50 and 400 Å can be studied by X-ray or electron diffraction (*7*). If the glasses are annealed at high temperature, the particles grow in size with time (at constant temperature) and may reach a diameter of over 1000 Å.

Comparison of spectral transmission curves from unannealed and annealed glasses (e.g., glass 1 in the table) shows a shift of the absorption edge to longer wavelength on annealing. The unannealed glass has an absorption edge at 340 nm and an absorption maximum at 775 nm; the latter is attributable to the presence of the Cu^{2+} ion (the glass has a bluish tinge). After annealing at 600°C, the absorption edge has shifted to about 390 nm ($\Delta\lambda$ = 50 nm) and the glass has become greenish in color. The Cu^{2+} absorption is unchanged by annealing.

While pure silver halides show absorption in the UV with features extending into the visible region (*1*), the absorption shifts to longer wavelength with increasing particle size.

The UV absorption in silver halides is due to an electronic transition from the valence band to the conduction band. Superimposed on this broad background are other, sharp absorption bands, in which the electron does not end up in the conduction band, but becomes coupled to a hole and can travel through the crystal lattice as an exciton (*1*).

The absorption edge of phototropic glasses shifts to longer wavelength with increasing annealing temperature and time, and also with increasing halide concentration. This verifies that the silver halide particulates are indeed responsible for the shift of the absorption edge in these glasses.

If these particles are allowed to grow beyond a size of about 300 Å, they begin to act as Rayleigh scattering centers. Beyond 2000 Å this leads to a noticeable cloudiness in the glass. Such large scattering centers, produced by extended, high temperature treatment, show all the normal crystalline properties of silver halides.

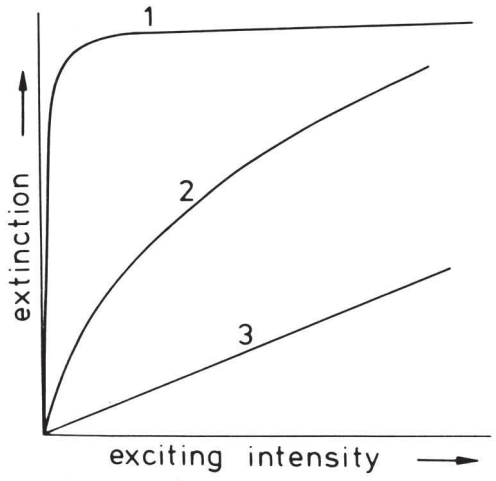

Figure 3. Effect of the thermal bleaching constant k_t on the equilibrium concentration of dark centers (C_s). Ordinate: extinction at equilibrium (at saturation transmission). From (*10*). Curve 1: very slow thermal bleaching ($k_t \approx 0$) C_s = const.; curve 2: phototropic glass; curve 3: fast bleaching $C_s \sim \Phi_s$ (see text).

Kinetics of Phototropism

Since the discovery of the phenomenon many kinetic formulations of phototropism have been proposed. However, like all formally kinetic descriptions, they give little insight into the microscopic processes involved (*8*, *9*).

A phototropic material is characterized by the maximum attainable optical density and by the regeneration speed. The rate of change of the concentration of dark centers with time (dc/dt) is proportional to the incident light intensity (Φ_e) and to the number of sensitive silver halide centers (Z):

$$dc/dt \sim Z \cdot \Phi_e \qquad (1)$$

The reverse reaction to colorless silver halide takes place simultaneously with rate proportional to the number of dark centers (c). Two processes are responsible for this reverse reaction: (1) optical bleaching or fading and (2) thermal bleaching. Optical bleaching is the conversion of silver back to the halide due to irradiation with visible light (550–750 nm). This involves electron transfer from the silver into the conduction band of the halide lattice.

Araujo and co-workers took the rate of optical bleaching as proportional to the light intensity (Φ_f) in the above spectral region. Thermal bleaching arises from the thermal motion of ions and holes and is one of the factors determining the position of equilibrium (and hence the saturation transmission).

If k_e, k_f, and k_t are the rate constants for the darkening reaction and for the optical and thermal bleaching, respectively, we can write the following equation for the rate of darkening:

$$dc/dt = k_e\Phi_e Z - (k_f\Phi_f + k_t)c \qquad (2)$$

These rate constants will be determined by the number and size of the light-sensitive centers. At equilibrium with $dc/dt = 0$, one obtains the saturation concentration (C_s) of dark centers:

$$C_s = k_e\Phi_e Z/(k_f\Phi_f + k_t) \qquad (3)$$

If k_t, the rate constant for thermal bleaching, is small, then C_s is independent of the light intensity, because the ratio of stimulating to bleaching light (Φ_e/Φ_f) is constant. If k_t is larger, it may become rate limiting. C_s is then proportional to the incident light intensity. This dependence can be seen in Figure 3.

The individual processes all show a strong temperature dependence. Most of the glasses do not darken at all above 80°C; the regeneration time and saturation extinction increase markedly with falling temperature. This strong temperature effect is due to changes in the silver ion mobility and to the increase in residence times of electrons and holes in a shallow potential well as the available thermal energy decreases with falling temperature.

The Phototropic Reaction

It is useful, when considering the mechanism, to keep in mind the analogous case of photography, where images are formed by the action of light on silver halide particles in a gelatine matrix (*11*).

When the silver halide photoconductor is irradiated ($\lambda \approx$ 500 nm), electrons and holes are produced in the conduction and valence bands, respectively (see Fig. 4).

In very pure AgX the electron/hole pairs recombine very rapidly. Photographically activated AgX therefore contains small amounts of silver and/or silver sulfide. These act as traps which collect the photoelectrons and thus become negatively charged. These negative charge centers are able to reduce interstitial silver ions to metallic silver. The holes generated along with the electrons are trapped by halide ions (X^-). The resulting halogen radicals (X·) are chemically "fixed" by the gelatine. The isolated silver atoms have only a short lifetime. Four to 10 of them from separate photochemical events diffuse together to form an aggregate. These aggregates on the surface of the halide form the latent image and act as nuclei for subsequent chemical intensification (development). The reducing agent in the developer can attack at these defects on the otherwise uniformly negatively charged halide grain, under the autocatalytic influence of metallic silver. The process of development gives an immense degree of image intensification from a few silver atoms to a macroscopic silver grain.

The processes occurring in the irradiation of a copper-containing phototropic glass have been summarized by Gliemeroth and Mader as follows:

$$Br^-(Cl^-) + h\nu \rightarrow Br^0(Cl^0) + e^- \quad (4)$$

$$Ag^+ + e^- \rightarrow Ag^0 \quad (5)$$

$$Cu^{2+} + e^- \rightarrow Cu^+ \quad (6)$$

$$Cu^+ + Ag^+ \rightarrow Ag^0 + Cu^{2+} \quad (7)$$

$$Cu^+ + Br^0(Cl^0) \rightarrow Cu^{2+} + Br^-(Cl^-) \quad (8)$$

$$Ag^0 \rightarrow Ag^{\square} \quad (9)$$

Atomic silver is precipitated according to reactions (5) and (7) and grows into microcrystalline $Ag^{\square}$ at the grain boundaries in the halide phase. As summed up by G. M. Schwab:

> The significant difference between the phototropic glasses and the photographic emulsion is that the anion here is an inorganic, amorphous giant polymer and that there is no acceptor such as nitrate or gelatine at hand. Radicals or radical anions produced when electrons are transferred to the silver ions cannot escape or be reduced [*8*].

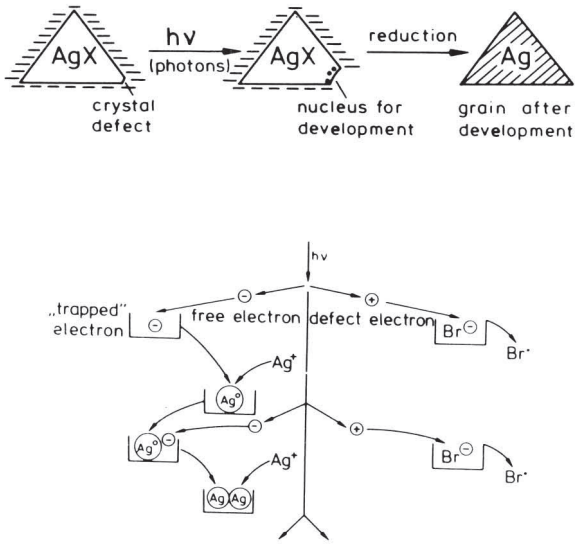

Figure 4. Schematic representation of latent image formation in photography and during development. From (*11*).

Unexposed phototropic glass appears green, but this impression disappears as $Ag^0/Ag^{\square}$ is formed. An absorption band emerges around 500 nm in the transmission spectrum. The position of maximum spectral intensity is a function of the particle size, structure, and composition of the halide phase and also of the halide type. The material can thus be "tailored" to have the desired spectral sensitivity in the short-wavelength visible and near-UV regions.

Additionally, the silver halide phase also contains low concentrations of components from the glass matrix. This leads to a shift of the absorption features to shorter wavelength; the band gap (between valence and conduction bands) increases with increasing foreign atom concentration. Much research effort is at present directed to increasing the sensitivity of phototropic glasses, for example by the addition of Ag_2S by analogy with photographic materials. The most important defects in silver halides are so-called Frenkel defects—a lattice vacancy with an ion in an interstitial site. Consequently, attempts are being made to influence the defect equilibria and hence the phototropic properties by substitution of two interstitial silver ions by one divalent cation (e.g., Ca^{2+} or Cd^{2+}). The Cu^+ ion is also able to occupy either lattice or interstitial sites. From this viewpoint the Cu^{2+}/Cu^+ system can be considered to have a sensitizing effect (see table).

Applications of Phototropic Glass

The ophthalmological uses as spectacle glass whose transmission changes in response to sunlight are well described in the patent literature (*12*, *13*).

Holography appears to be an interesting new area of application (*14*), because the resolution is an order of magnitude better than that of photography, which is limited by the grain size (*15–17*). To be useful as a data storage medium, the hologram must be stable, rapidly recordable (10^6 bits/s), and possess good regeneration properties. Possible methods of erasing stored data are currently under discussion. These include IR lasers or simply heating by means of a transparent, conductive tin oxide coating on both sides of the glass. The application of a voltage can reduce the regeneration time by a factor of 50 (*1*). Bräuchle has reviewed the photochemical aspects of holography (*19*).

Experiments with Phototropic Glasses

Photokinetics of a Glass Sample

Materials required: Phototropic glass (e.g., a sample from Schott A.G., Mainz, W. Germany); solar cell (e.g., BPY 47); strip chart recorder with variable zero offset; high pressure mercury vapor lamp; He-Ne-laser ($P > 0.2$ mW); iris diaphragm; hot plate; beaker.

The experimental arrangement is illustrated in Figure 5. The glass sample, suitably mounted, is irradiated with the mercury lamp. The iris diaphragm is necessary in order to restrict the light beam diameter.

The solar cell output is connected directly to the input of the strip chart recorder and the zero offset adjusted to give an appropriate starting value. The experiment should be carried out in a darkened room and the sample kept in the dark for at least an hour beforehand. Rapid regeneration is assured by warming the sample for 10 min in a water bath at 90°C before the experiment (also performed in the dark). Additionally, to ensure constant light output, the experiment should not be started until the mercury lamp has stabilized by running for 15 min.

When the adjustments are complete (without the target) the glass sample is inserted into the light path and the darkening curve obtained. A typical recorder trace is reproduced without any "tidying up" in Figure 6, curve A. The form is characteristically exponential and may be analyzed with the usual techniques for a first-order reaction (*8*).

If a similar experiment is performed on the regenerated sample using the laser instead of the mercury lamp (Fig. 6, curve B) no change

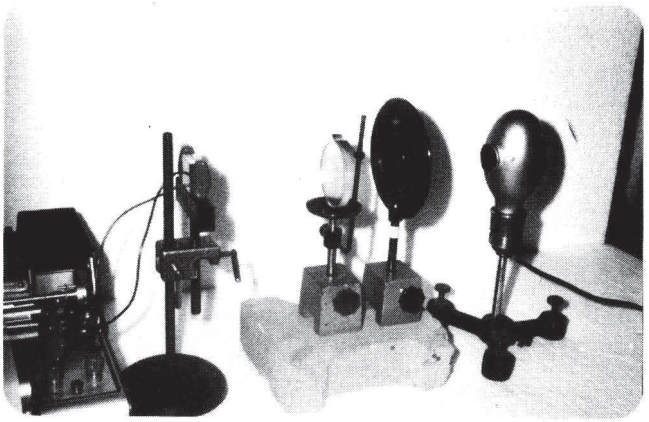

Figure 5. Experimental setup for investigation of darkening kinetics. Left to right: strip chart recorder, silicon cell, glass sample, iris diaphragm, high-pressure mercury vapor lamp. From (*18*).

in transmission is observed. Evidently the light from a He-Ne-laser at 632.8 nm causes no darkening of the glass (*18*), and is therefore suited to an investigation into regeneration. The bleaching curve (thermal + fading) can be obtained by shining the laser through a previously darkened sample on to the silicon cell. The iris diaphragm is not needed in this experiment due to the small divergence of the laser beam. A typical recorder trace is reproduced in Figure 6, curve C.

Temperature Dependence of the Phototropic Reaction

Materials required: same as those in the previous experiment, with the addition of a transparent Dewar vessel and liquid nitrogen.

To investigate the effect of temperature on the regeneration, the glass sample is placed in the Dewar filled either with water at different temperatures or with liquid nitrogen and inserted into the light path. Continuous measurements at liquid nitrogen temperature can be made only if precautions are taken to prevent the formation of frost on the sides of the Dewar. One solution is to glue a plastic tube to the side of the Dewar, connecting the other end suitably to the laser. The reduced humidity inside the tube allows investigation of optical bleaching down to −196°C (the temperature of liquid nitrogen). Alternatively, transmission measurements are made from a "staircase" curve obtained by periodically wiping the frost from the sides of the Dewar.

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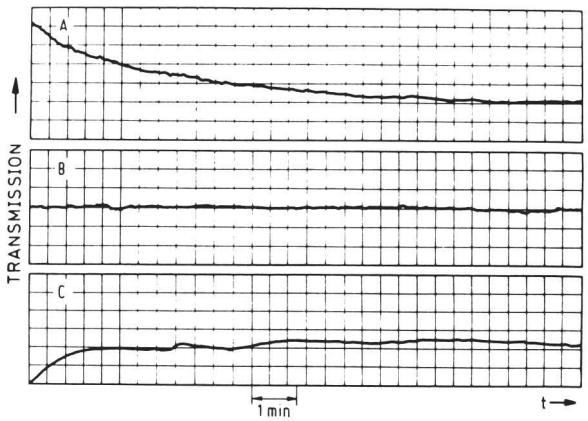

Figure 6. Curve A: reduction in transmission during irradiation of a phototropic glass with a high-pressure mercury vapor lamp. Curve B: transmission of a regenerated glass sample during irradiation with a He-Ne laser. Curve C: thermal and optical bleaching of a glass sample previously darkened to saturation transmission by a mercury lamp. (T = room temperature, sample thickness = 8 mm). From (*18*).

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