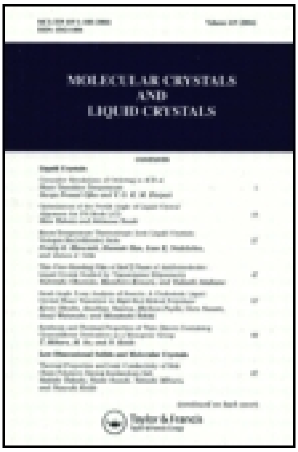

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INORGANIC PHOTOCHROMIC SYSTEMS

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Abstract The excited states of many organic molecules are sufficiently long lived so that excitation gives rise to a change in the absorption spectrum that persists for seconds or even longer. The author is unaware of any perfect crystal for which this is true. Vacancies are essential to the appearance of photchromism in alkali halides and sodalite crystals. Changes in absorption spectrum have accompanied charge transfer reactions between two impurities in titanate and calcium fluoride crystals. Photochromism has been observed in suspensions in glass of crystals too small to scatter light as well as in homogeneous glasses.

INTRODUCTION

An electron in an excited state absorbs light of a different energy than one in the ground state. Electronic excitation, therefore, leads to a change in the absorption coefficient as a function of wavelength which is called photochromism. For many applications of photochromic materials, the change in absorption coefficient which accompanies electronic excitation must persist for seconds or longer.

Because the lifetime of an excited electronic lifetime is very long compared to vibration times, atomic rearrangements can occur if the electronic excitation causes a significant change in the forces acting on the atoms. This is common in small isolated molecules in which the excited electron is associated with a particular bond. Sometimes the changes in atomic configuration strongly retards the return of the system to its initial state and the photoinduced change in absorption coefficient is sufficiently long lived for many applications.

Isomerization and tautomerism are examples of such a reconfiguration which can occur when organic molecules are irradiated. The long lived changes observed in small isolated molecules can also be observed in crystals if the excited electron is associated with a single bond. This is the case when very weak forces such as Van der Wall's forces are responsible for the crystal formation. Such crystals are not uncommon in organic systems.

In the inorganic systems of interest, the forces leading to crystal formation are sufficiently strong so that electronic states are strongly delocalized. In other words, excited electrons are not associated with any particular atom or bond. They exists everywhere in the crystal with equal probability. Thus, electronic excitation in perfect crystals does not cause atomic displacements large enough to cause long lived changes in the absorption spectrum when the crystal is irradiated. For that reason, localized electronic states associated with impurities or defects are essential to the observation of photochromism in inorganic systems.

PHOTOCHROMIC CRYSTALS

In inorganic crystals, other than those like silane or xenon which are held on lattice sites by Van der Waal's forces, overlap is strong and wide energy bands are formed. Band gap radiation produces electron-hole pairs. Since neither the electrons in the conduction band nor holes in the valence band are localized in a perfect crystal, electron-hole recombination is very rapid and photochromism is not observed. In order for recombination to be retarded sufficiently for photochromism to be observed, it is necessary that the crystal contain defects which introduce electron trapping states in the forbidden gap as well as defects which introduce hole trapping states. Transition metal ion impurities, rare earth ion impurities or oxygen vacancies serve as trapping states in some systems.

Several of the most studied photochromic crystals are described briefly in this section. They illustrate the kinds of defects that give rise to gap states and that make photochromism observable. The examples also provide a basis of comparison of the performance parameters of organic and inorganic photochromic materials.

Alkali Halides Photochromism in the alkali halides is predicated on the use of electromagnetic radiation to convert one type of defect or color center to a different defect having a different absorption spectrum. Color centers in alkali halides can be produced by a variety of techniques, the most important of which are additive coloration, electroytic coloration and exposure to ionizing irradiation.

An excess of either alkali or halogen is introduced by heating the crystal to a high temperature in the vapor of one of the constituents. Exposure to alkali vapors produces a crystal with alkali atoms on cation lattice cites and anion vacancies. The free energy of the system is decreased by ionization of the alkali atom and the subsequent trapping of the electron at a cation vacancy. The trapped electron, called an F center, gives rise to an absorption band whose peak position is determined primarily by the lattice parameter of the crystal.

The F center is the defect which is most convenient for probing the photochromic material. The F center has a hydrogenic set of states. The absorption band corresponds to a transition from the $1s$ to a $2p$ state of a square-well-like potential. Because both the $1s$ and the $2p$ wavefunctions are confined to the vacancy, they experience a strong overlap. Therefore, an oscillator strength near unity is observed. An absorption coefficient as high as $100cm^{-1}$ is obtained with a concentration of only 10^{17} centers per cubic centimeter. At temperatures above $140^{o}K$, the $2p$ electron is ionized into the conduction band with near unit efficiency by absorption in the F band.

Once released, the electron can be trapped by another F center, thereby forming a new center, called an F' center, with two electrons trapped at an anion vacancy. Optical excitation in the F' center promotes the electron directly into the conduction band and can give rise to two F centers. Since two F centers are formed or destroyed by an interconversion to F' centers, the quantum efficiency is bounded by two rather than unity. At low enough temperature, non-destructive readout is possible by interrogating the F center. Fatigue is observed because of the possible formation of other kinds of defects such as the aggregation of F centers, called an M center.

Photochromic Sodalites Sodalite is a crystal having the stoichiometry $3Na_2O$ $3Al_2O_3 \cdot 6SiO_2 \cdot 2NaCl$. Natural Hackmanite, a mineral having the same structure as sodalite with a partial replacement of halogen atoms by sulfur, can be darkened by long wavelength UV and optically bleached by visible light. The color center responsible for the induced absorption is an F center. Although there seems to be agreement that sulfur is the electron donor, the form of the sulfur has not been firmly established.

Photochromic Titanate Crystals Although the author is unaware of any case in which charge transfer bands between transition metal ions or between rare earth ions can lead to photochromism in glasses, that mechanism has been observed in crystals. Prototypical of this phenomenon is the photochromism observed in $SrTiO_3$ or TiO_2 doped with iron and molybdenum. Faughnan and Kiss[1] used optical and ESR spectra to show that charge transfer from Fe^{+3} to Mo^{+6} gave rise to the formation of Fe^{+4} and Mo^{+5} ions. The latter ions are responsible for the photoinduced absorption bands in the visible. The thermal decay time in Fe/Mo doped $SrTiO_3$ at 300^oK is several minutes. In TiO_2, the decay time is very short and the spectra must be measured at 77^oK. It is believed that both Fe^{+3} and Mo^{+6} occupy Ti^{+4} lattice sites. Mo^{+6} partially charge compensates the Fe^{+3}.

Photochromism In Calcium Fluoride Crystals Photochromic effects can be observed in calcium fluoride doped with La, Ce, Gd, or Tb and additively colored by baking in calcium vapor. The additive coloration does not simply reduce the rare earth ion to its divalent state. A complex state that may be described as a strongly interacting divalent ion and a nearest neighbor F center, simply called an REF center, is formed.

UV exposure ionizes the REF center and the electron is trapped by an isolated trivalent rare earth ion. Both the REF^{+1} and the RE^{+2} have absorption bands in the visible which are responsible for the photoinduced coloration. Irradiation in the RE^{+2} bleaches the system to its original state. Staebler and Schnatterly[2] demonstrated that the REF center is anisotropic. As a result, linear dichroism can be produced by exposing the sample to linearly polarized light.

The quantum efficiency for photoinduced coloration is about 10% for 400nm irradiation but increases at shorter wavelength. Optical bleaching at 550nm requires about $1J/cm^2$ for a unit change in optical density. The largest absorption coefficient change observed is about $50cm^{-1}$. Thus, practical use of these materials is limited to about 200 microns. The efficiency of the optical switching is independent of temperature.

The systems discussed above illustrate the importance of defects which exist in the bulk of certain crystals causing them to be photochromic. Surface states can also give rise to localization. Suspension of minute crystals having a high density of localized surface states in an inert matrix can also give rise to photochromism. Such systems are exemplified by glasses containing crystallites of silver chloride or cuprous chloride. These systems will be discussed in some detail in later sections.

SINGLE PHASE PHOTOCHROMIC GLASSES

Electronic states in amorphous solids or glasses, like those in crystals, form quasi-continuous bands separated by ranges of energy which are inaccessible. Unlike the states in a perfect crystal, some of the states in an amorphous solid do not extend over the entire system but are localized on specific atoms. If the localized state populated by the absorption of a photon differs sufficiently in energy from all of the extended states, it may, like defects in crystals, stabilize the excitation and give rise to photochromism.

Although it is not often described as a photochromic material, amorphous arsenic sulfide illustrates the effect discussed in the last paragraph. Absorption of a photon greater than the band gap gives rise to photodarkening. Although the darkening is not reversible at room temperature, it can be bleached by heating the material to the glass transition temperature. It can also be bleached at room temperature by irradiation with long wave light. According to Owen et al[3] these effects are not observed in crystalline arsenic sulfide. Because the electronegativities of arsenic (2.2) and sulfur (2.4) are so similar, it is plausible that these glasses contain a significant degree of chemical disorder (e.g. sulfur-sulfur bonds) or *valence alternating pairs*[4].

A small number of photochromic glasses are found among the oxide glasses. The strength of the bond between the metalloid atom and the oxygen atom in these systems is strong enough so that chemical disorder is negligible. The large difference between the electronegativities of oxygen and the metalloid atoms suggests that valence alternating pairs are not present in significant concentrations. The variation in bond angles found in glasses but not found in crystals can give rise to localized states. The energy of these states is almost certainly less than a few kT at room temperature and so electrons in such states are easily thermalized into the bands of extended states. It is probably for these reasons that so few examples of photochromism are found in oxide glasses.

Cohen and Smith[5] reported that strongly reduced silicate glasses are photochromic. Darkening sensitivity is enhanced by cerium, europium, or zirconium. A darkening sensitivity of about $100mJ/cm^2/dB$ was reported for an eight millimeter sample of glass doped with europium. Fading was essentially complete in five minutes after cessation of irradiation. All of these glasses show fatigue in that the level of darkening decreases with repeated cycling. The fatigue is associated with an increase in the fade rate. No suggestion about the nature of the absorbing center has been presented in the literature. However, it is reasonable to speculate that the strong reducing conditions employed lead to oxygen vacancies and that photochromism is related to trapping of electrons at the vacancies, just as it is in the glasses discussed in the next paragraph.

Photochromism has been observed more recently in calcium aluminate glasses which were melted under strongly reducing conditions[6]. These glasses are first melted in air, quenched and remelted in graphite crucibles under a nitrogen atmosphere. The glasses are ordinarily light yellow as made and they turn dark blue or grey under UV irradiation. In undoped glasses, the maximum in the spectral sensitivity curve is close to the transmission edge of the optical spectrum before illumination. In glasses doped with cerium another peak in the sensitivity curve appears at about 340nm, the Ce^{+3} absorption peak. The correlation between the induced absorption bands and the photoinduced ESR signals suggests that the induced absorption can be ascribed to an electron trapped at the site of an oxygen vacancy surrounded by Ca^{+2} ions. It seems plausible that the photochromism observed in reduced silicates might also involve electrons trapped at oxygen vacancies.

Meiling[7] described a family of homogeneous glasses based on the $CdO-B_2O_3-SiO_2$ system that are photochromic and show no fatigue. Stable glasses can be made with a wide range of ratios of silica to boric oxide, if the mole percent of cadmium oxide is between 45 and 65. The shape of the induced spectrum was very nearly flat throughout the visible spectrum. Typically an energy density of the order of $1J/cm^2$ is required to obtain 2dB of darkening in a two mm thick sample. Several hours are required for complete bleaching of these glasses.

The nature of the photoinduced color center is not known with certainty. However, spin resonance measurements indicated a reasonably strong correlation between the induced absorption and the strength of the Cd^{+1} spin signal. Presumably, variability in the coordination of cadmium by oxygen gives rise to electron trapping at a small number of cadmium sites.

GLASSES CONTAINING CRYSTALLITES

Armistead and Stookey[8] observed that when silver, copper, and halides were included in the batch from which certain borosilicate glasses were melted, photochromism was observed. These investigators speculated that the photochromism was a result of the photolysis of silver halide crystallites and that the photolysis of the silver halide in these glasses was similar in many respects to the photolysis of the silver halides in photographic emulsions. It can be described schematically by the following equations.

$$Cl^- + h\nu \Rightarrow Cl^o + e^-$$

$$Ag^+ + e^- \Rightarrow Ag^o$$

$$nAg^o \Rightarrow Ag_n^o$$

$$Cl^o + Cu^+ \Rightarrow Cl^- + Cu^{++}.$$

All steps except the last are common to both systems. In photographic emulsions, the last step is replaced by

$$Cl^o + M \Rightarrow MCl$$

where MCl represents the reaction product of the halogen atom and the organic matrix M.

Photochromic glasses are formed by any of the standard glass forming techniques from melts which contain, in addition to standard glass forming materials, salts of silver and halides. In most cases the glass item is not photochromic as initially formed. The glass must be held at some elevated temperature ($\sim 600^oC$) in order to precipitate the silver halide crystallites and render the object photochromic.

Silver halides can be precipitated to produce transparent photochromic glasses from a wide range of host glasses. Consequently, the physical properties of the host glasses can be varied over a wide range. Variations in either composition or thermal history can be used to produce a wide range of photochromic properties. A small amount of copper increases the darkening sensitivity by several orders of magnitude and is included in almost all transparent photochromic glasses. Furthermore, the concentration of copper in the silver halide crystal has a profound effect on the fade rate and on the temperature dependence of the steady state level of darkening. Thermal fade times range from seconds to many years. The level of darkening observed at equilibrium is very sensitive to temperature in glasses which fade moderately fast and very insensitive to temperature in those which fade very slowly at room temperature. Commercially available photochromic sunglasses darken to about 25% transmittance at 70^oC in sunlight and fade to about 65% in five minutes after the cessation of irradiation. Complete fading is achieved in about an hour.

It is not possible to specify precisely the fade rate of a specific sample of glass because the fade rate is not a unique function of the temperature and the level of darkening. The rate at which a glass fades from a given level of darkening depends on the duration and on the intensity of the irradiation. If the temperature is not maintained at a constant value during the entire darkening and fading process, the fade rate depends on the temperature history as well as on the instantaneous temperature.

Borrelli et al.[9,10] describe the production of optical anisotropy by the optical bleaching of photochromic glasses with polarized light. In the latter reference, they also describe color adaptation. For reasons that are not completely understood, many photochromic glasses exhibit a memory effect. After a glass has been partially optically bleached so as to exhibit polarizing power or color adaptation and then allowed to thermally fade so completely that no absorption is measurable, a second exposure to UV causes the glass to redarken and to regain its polarizing power or adapted color. However, the memory is not complete. Repeated darkening and thermal bleaching eventually causes loss of most of the memory. Heating to a temperature above 200^oC causes rapid and complete loss of memory.

Araujo[11] disclosed transparent photochromic glasses which contain crystallites of cuprous halides or mixed crystallites of copper and cadmium halides. These glasses are similar in many ways to those containing silver halide crystallites. The kinetics of darkening and thermal fading are similar to those of the silver halides. However, no optical bleaching has been observed for any of the copper halide glasses. This characteristic provides non-destructive readout capability but it precludes selective erasure.

Kinetics Of Bleaching In sufficiently fluid systems, reactants are so mobile that chemical reaction does not alter the spatial distributions of reactants other than to uniformly diminish them. In many solid state reactions, that is not the case. In the bleaching reaction of silver halide in photochromic glass, the reaction leads to a significantly non-uniform spatial distribution of the reactants.

The photolysis of silver halide was described above as the transfer of an electron from a Cu^{+1} ion to a Ag^{+1} ion, thereby forming Cu^{+2} (trapped holes) and Ag^0 (trapped electrons). The silver atoms aggregate to form silver colloids on the surface of the silver halide crystallites[11]. Cu^{+1} ions and Cu^{+2} ions can both migrate.

Bleaching occurs by means of an electron tunneling from the silver colloid to a Cu^{+2} ion and the transfer of a Ag^{+1} ion from the positively charged colloid into the silver halide crystal. However, tunneling cannot occur unless the Cu^{+2} ion is close to the silver colloid. The supply of Cu^{+2} ions near the colloid is maintained by their diffusion. Thus, the distribution of Cu^{+2} ions is not uniform in space because the tunneling depletes those near the site of the silver colloid. It is the interaction of tunneling and diffusion that gives rise to the peculiar temperature dependence cited above.

In the examples of inorganic photochromic systems discussed, defects give rise to localized states which can trap holes or electrons. The low mobility of these trapped carriers and the very high probability of recombination when they are sufficiently close to each other give rise to effects not observed in gas phase reactions. The most important of these is that the rate of the chemical reaction is not uniquely determined by the average concentrations of the reactants[12]. As a consequence, the measurement of the bleaching rate in one experiment is of limited value for predicting the rate in another experiment. As a further consequence, the observed net darkening rate cannot be corrected to obtain the total darkening rate by simply adding the fading rate observed at the same level of darkening during the fading cycle. Thus, it is very difficult to determine the quantum efficiency of darkening in photochromic glasses which contain silver halide or in almost any inorganic photochromic system.

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