

PHOTOCHROMICS

One may "read", "write" and "erase" photochromic materials using light of different frequencies.

Lattice defects and impurities are responsible for this potentially useful phenomenon.

ZOLTAN J. KISS

A GREEN MATERIAL MAY TURN BLUE; a pale blue material may turn purple and a white material may turn red as different colors of light shine upon them. This photochromic effect is a property of certain types of inorganic materials. Among those that have been studied are single crystals of calcium fluoride doped with rare-earth elements, and strontium titanate doped with transition metals, and the alkali halide, potassium chloride. If these materials are to be used as light-sensitive media, their sensitivity to light, their rate of switching color and their resolution are of particular importance. Once the photochromic mechanism is completely understood,

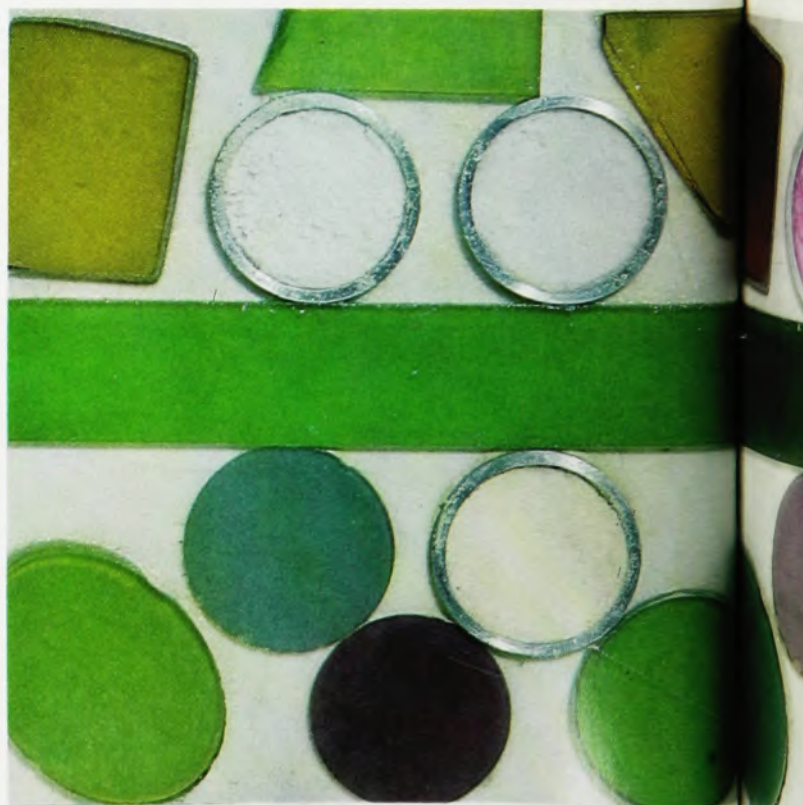
its technical applications may range from computer memories to three-dimensional television.

The word "photochromic" derives from two Greek words meaning light and color. Photochromic materials are materials that change color in a reversible way under illumination by light. The reversible process can take place either in the dark under thermal excitation or by illumination with light of a different frequency. Because the color change is reversible, photochromic materials offer greater promise than those where an absorption band can be permanently bleached out ("photobleach") or can be permanently induced ("photocolor").

The first report on photochromic materials in the technical literature occurs around the turn of the century, describing the color change of certain paint under different light conditions. Some preliminary work was carried out on various powders and on naturally occurring minerals, and this work is summarized in a review article.¹ Over the past 20 years considerable work has been devoted to organic photochromic materials, and much of this work is covered in two recent review articles.^{2,3} In organic systems the reversible color change usually depends on light-induced molecular rearrangement of complex molecules.

The study of inorganic photochromic

INORGANIC PHOTOCHROMIC-CRYSTALS, titanates, fluorites and hackmanites (a) in thermally stable state, (b) about one minute after ultraviolet irradiation and (c) after irradiation through a mask. This figure shows the variety of colors and visual contrast available. —FIG. 1



mic materials for the solid-state physicist consists primarily of the study of photoinduced charge transfer between deep-lying impurity levels. The deep levels may either result from impurities such as transition metals or rare-earth elements incorporated into wide bandgap insulating materials, or they may result from lattice defects or combinations of both. The phenomenon cannot be adequately described by the band theory or by the crystal field theory applicable to isolated ions; a hybrid description of the two techniques using molecular-orbital types of wave function is necessary.

PHOTOCHROMIC MECHANISM

Photochromic materials will possess different absorption spectra depending on conditions of illumination. Figure 2 shows the absorption spectra of an idealized photochromic material. In state A of such material we have at least two absorption bands, one at 400 nanometers in the figure and one at 600 nm. When light is absorbed at 400 nm the absorption spectrum characteristic of state A disappears, the color changes and a new absorption spectrum appears as shown by the colored curve for state B. When light is absorbed in state B by the 500-nm band, the initial absorption spectrum of state A returns. Even in

the dark state B is not stable but may return to state A through thermal excitation. The second absorption in state A at 600 nm has the characteristic that when light is absorbed by the band, the material remains in state A and there is no photochromic color change.

By the function of the different absorption bands we might call the 400-nm absorption band the "erase" band because it erases the "read" band, the 500-nm band of state B the "write" band and the 600-nm band of state A the "read" band, having non-destructive readout capabilities.

A simple model

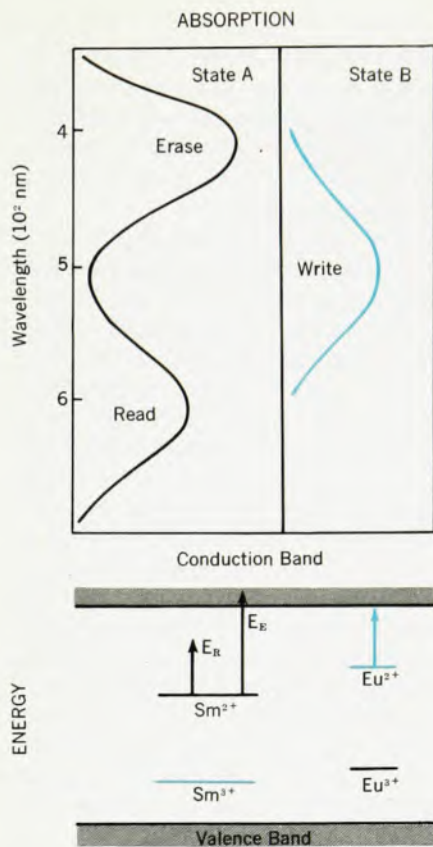
A schematic diagram of a solid-state phenomenon that could lead to these absorption characteristics is shown on the same figure. Let a high bandgap material such as calcium fluoride contain two impurities, for example, Sm^{2+} and Eu^{3+} . The black lines mark the positions of the ground states of these isolated impurities in the forbidden gap of the host material. The position below the conduction band indicates the amount of energy needed to lift an electron off the ground state of an impurity and place it in the conduction band. The example actually quoted here, based on the simultaneous presence of samarium and europium in calcium fluoride, has been

observed previously.⁴ However, the absorption spectrum shown in figure 2 is not the absorption of samarium and europium but only a schematic diagram to illustrate a type of charge-transfer mechanism leading to photochromism.

Let us further assume that the color of the material comes from the divalent rare earths and that the trivalent rare earths have no apparent absorption in the visible region of the spectrum. Then in state A the absorption arises from Sm^{2+} , the "erase" band overlapping the conduction band and the "read" band being in the forbidden gap. When, in state A, the Sm^{2+} ion absorbs "erase" light, the electron is excited into the conduction band, and it can be retrapped by any other electron trap, in this case by Eu^{3+} . But when the electron is transferred from the samarium to the europium ion it leaves Sm^{3+} and Eu^{3+} becomes Eu^{2+} . So state B corresponds to the new pair of impurities, Sm^{3+} and Eu^{2+} , and the color of the new state results from the Eu^{2+} ion.

If the "write" light is now absorbed by Eu^{2+} , lifting the electron off the Eu^{2+} ion back into the conduction band, this electron can be retrapped by Sm^{3+} , reconverting the system into state A, that is to the Sm^{2+} and Eu^{3+} pair of impurities. This then is a possible solid-state mechanism leading to





POSSIBLE PHOTOCHROMIC MECHANISM. Absorption of state A (black) changes to that of state B (color) when an electron is transferred from Sm^{2+} to Eu^{3+} . One may "read", "write" and "erase" with photons of energies E_R , E_W and E_E . —FIG. 2

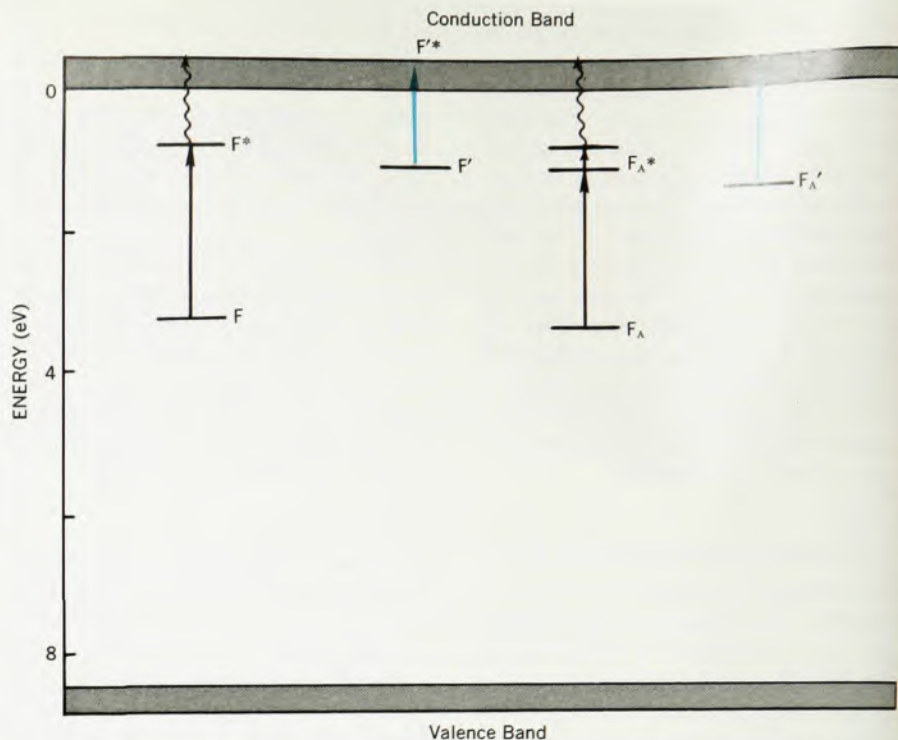
photochromic absorption characteristics.

Predictions of the model

Some of the factors that determine the characteristics of photochromic materials can be predicted by this model.



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COLOR CENTERS in potassium chloride give rise to various energy levels. Photoexcitation of the F, or color, center (black arrows) is followed by thermal excitation (wavy arrows) into the conduction band. The F_A centers, resulting when an F center is near an impurity, have nondegenerate excited levels. The F' and F_A' levels, corresponding to an electron trapped at a color center, may be excited directly into the conduction band (colored arrows). —FIG. 3

For example, the lifetime of state B in the dark is determined by the trap depth of Eu^{2+} below the conduction band and will be a strong function of temperature. The different colors of the materials in the different states will be determined by the absorption bands of the impurities and their positions in the bandgap. Also according to the simple model the photochromic charge transfer will be accompanied by photoconductivity. The photochromic sensitivity (a measure of the number of photochromic centers switched per number of photons absorbed) is expected to vary with the energy of the exciting light and will depend on the concentration of the various valence states of the different impurities. Furthermore this sensitivity and the ultimate attainable concentration of the different photochromic centers also depend on the overlap of the "write" and "erase" absorption bands. These properties have in fact all been observed.

COLOR CENTERS

Our understanding of one type of inorganic photochromic material comes

from the interest by several workers in the study of color centers.⁵ These color centers, called "F centers" after the German word, "Farbzentren", are negative-ion vacancies where an electron has been trapped. The photochromic process in alkali halides results from the photoexcitation of these F centers.

When an electron from an F center is lifted into the excited F^* state (figure 3) by absorbing 500-nm light, there is a finite probability, depending on the temperature, that the electron assisted by thermal phonons will ionize into the conduction band. This electron can be trapped at temperatures below 200 K by an F center, forming the F' center. The F' center then consists of two electrons trapped at a negative ion vacancy. The position of the ground state of the F' center can be seen in figure 3. Experimental and theoretical studies have delineated the nature of the two absorption bands. The main absorption of the F center is caused by a $1s-2p$ type of transition of an electron in a three-dimensional square-well potential. Several refinements of the theory account for the higher excited states

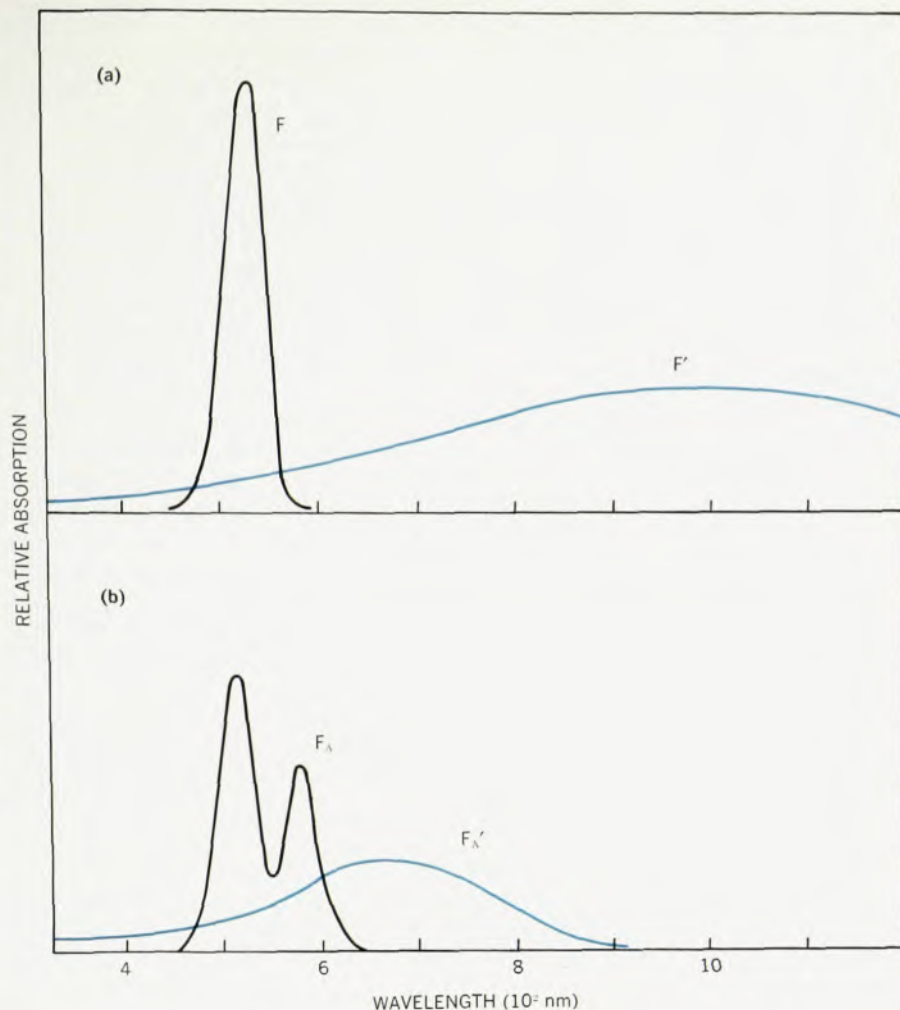
and their interaction with the conduction band. Experimentally, absorption, photoconductivity, the Hall effect and field-ionization measurements confirm the model suggested by figure 2.

The predominant absorption band of the F center in potassium chloride is shown in figure 4a. There are other weaker absorptions on the high-energy side of this band that are not shown in this figure. The broad absorption band associated with the F' center, shown by the colored line, results from a direct charge transfer from the ground state of the F' center into the conduction band. At sufficiently high temperatures this ionization can also take place thermally. Hence the F' center can only be observed at low temperatures.

A more stable version of these centers occurs when the centers are trapped near a lattice imperfection or an impurity. The absorption spectra of such modified centers is shown in figure 4b. In this case, the F_A and F'_A centers are the corresponding centers trapped next to a sodium ion replacing a potassium ion in the potassium-chloride lattice. This perturbation has several effects. The noncubic electric field component of the distorted lattice removes the degeneracy of the excited 2p state, leading to two main absorption bands for the F_A center. Furthermore the position of the ground state of the F'_A center is lowered in the forbidden gap of potassium chloride, leading to higher temperature stability of the F'_A center and higher energy absorption peak of the F'_A band. Several versions of the modified F center have stable photochromic states at room temperature and have been used commercially.⁶

Practical difficulties

After several years of excellent academic color center research, practical technological benefits are in sight through its photochromic properties. However, there are several practical difficulties of such material. The first of these is fatigue. As the electron is shuttled back and forth between the two F centers, the absorption spectra of figure 4a diminish, and a new stable absorption band is created at longer wavelength. This absorption arises from the M center, which is formed as the negative-ion vacancy diffuses to the F' center. The M center is then like a hydrogen molecule, composed of two F centers, and is stable against irradiation by light.



ABSORPTION SPECTRA. (a) The stable peaked absorption spectrum of potassium chloride (black) changes to the broad spectrum (color) after formation of an F' center. (b) The spectrum of potassium chloride doped with sodium illustrates the removal of the degeneracy of the F^* levels (black) and the broad spectrum (color) of the F'_A levels.

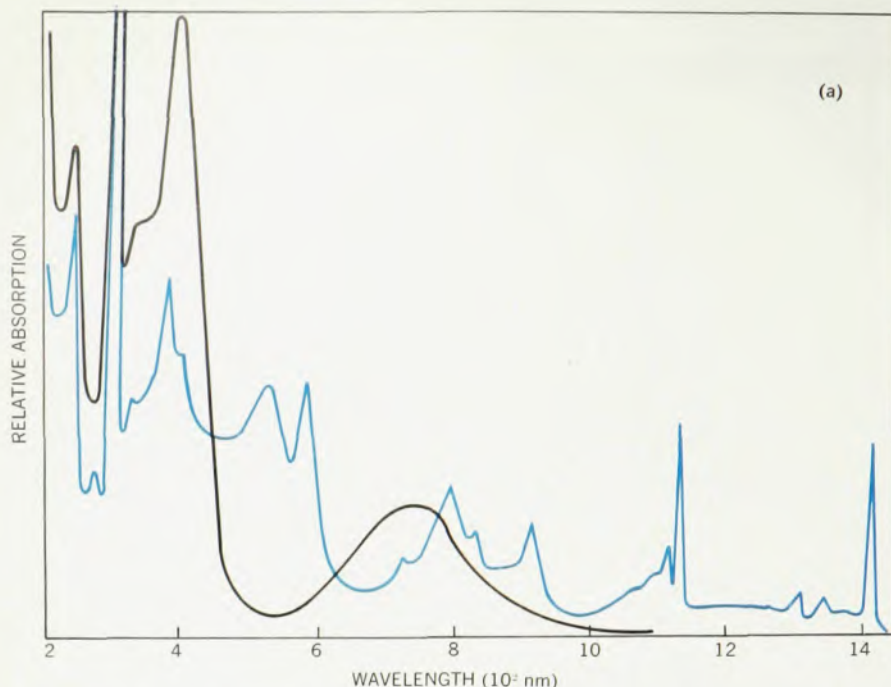
—FIG. 4

The second difficulty with color centers in alkali halides as photochromic materials is the relatively low concentration of centers. At concentrations greater than 10^{18} centers/cm³, various color-center complexes are formed that do not lead to photochromic effects. To overcome some of these difficulties, the color changes can be associated with known impurities instead of lattice defects.

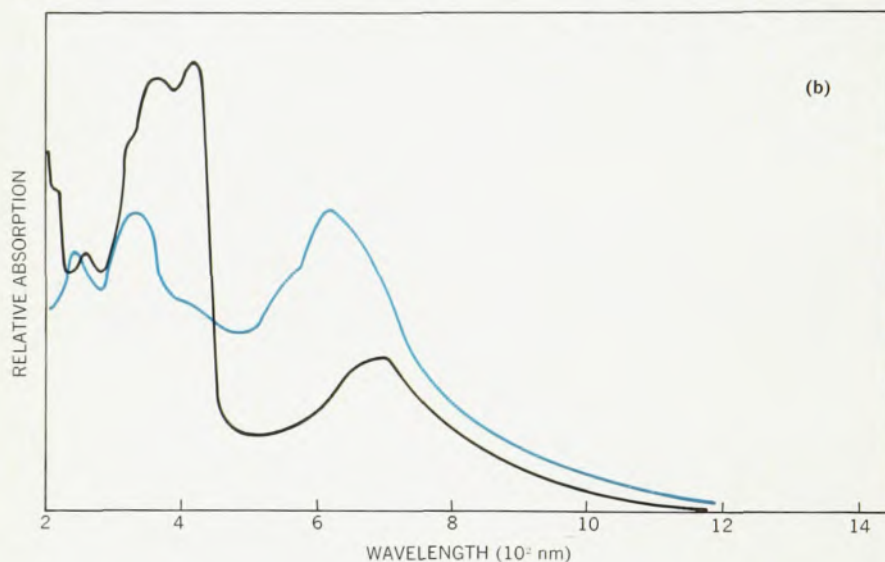
RARE-EARTH IMPURITIES

Laser materials constructed of calcium fluoride doped with rare-earth elements exhibit color change under strong illumination. This characteristic, undesirable for the laser, was exploited for the photochromic effect. Four of the rare-earth elements, lanthanum, gadolinium, cerium and terbium, when treated under reducing

conditions, showed efficient large photochromic color changes at room temperature.⁷ Donald S. McClure and I predicted that these impurities have a 5d ground level in the trivalent state,⁸ contrasted with the 4f ground level of the other divalent rare earths. Figure 5a shows the absorption spectra of photochromic calcium fluoride doped with cerium at 78 K. In the thermally stable state, the absorption spectrum has two peaks, at 400 nm and at 700 nm, somewhat similar to the F_A absorption of figure 4b. After irradiation with light of wavelength less than 450 nm, the absorption spectrum changes to the one drawn with the colored line. David Staebler and I identified⁹ this spectrum as that of Ce^{2+} . The various relatively strong sharp bands originate from transitions of the electrons of the ground-state 4f5d configuration to the levels of the



DOPED CALCIUM FLUORIDE in the thermally stable state (black) and in the induced photochromic state (color). Impurities are (a) cerium at 78 K and (b) lanthanum at 300 K. —FIG. 5



excited $4f^2$ configuration. The thermally stable spectrum returns after irradiation by light of wavelength greater than 450 nm.

Figure 5b shows the two photochromic absorption spectra for calcium fluoride doped with lanthanum at 300 K. The absorption spectrum of the thermally stable state is very similar to the absorption spectrum of calcium fluoride doped with cerium; it has the two characteristic absorption bands at somewhat different frequencies. However, the ultraviolet-induced absorption is quite different from that of the cerium-doped materi-

al. Instead of the sharp line structure, there is a main broad absorption band at about 570 nm.

The model for the photochromic mechanism is only partly complete. In the case of calcium fluoride doped with cerium, the reducing treatment creates some type of color centers associated with Ce^{3+} , leading to the two broad absorption bands of the thermally stable state. The ultraviolet irradiation ionizes these centers. The released electrons will be trapped by trivalent cerium ions to produce Ce^{2+} . This process has been confirmed by observation of the decrease

in the Ce^{3+} absorption⁹ and identification of the induced Ce^{2+} bands. During the light-induced reverse process, the electron is ionized off the Ce^{2+} and returns to the original site. Photoconductivity measurements by Philip M. Heyman identified the electronic process in both directions giving an energy depth of the order of 3 eV for the thermally stable depths and 2.0 eV for the Ce^{2+} .

Two possible processes

The exact nature of the thermally stable center is not yet known. Linear dichroism measurements indicate that the centers are aligned along equivalent (111) directions and are like an F center (or similar more complex centers) associated with the rare earth. However, in the induced state at least two parallel processes are possible. The first one was illustrated by the creation of the divalent rare earth as in the case of Ce^{2+} , but there is another possible center created as in the case of lanthanum (figure 5b), leading to a single broad absorption band in the visible region of the spectrum. This broad band was observed for all four photochromic rare earths, the peak positions being different for the different rare earths.

Thus, in the case of calcium fluoride doped with rare-earth elements, the photochromic process is determined by at least one controllable impurity, with its own internal absorption. But associated lattice defects and color centers still play an equally important role. The absorption caused by these internal transitions (for example, the $4f-4f$ or $4f-5d$ transitions of Ce^{3+} and some of the $5d-4f$ transitions of Ce^{2+}) can be used to interrogate the sample with light without leading to charge transfer and thus destruction of the information (nondestructive readout).

TRANSITION-METAL IMPURITIES

Charge transfer between two controllable impurities is demonstrated in photochromic materials made of strontium titanate doped with transition metals. Strontium titanate is a more covalent insulator than the alkali and alkali-earth halides and has a lower bandgap than, for example, calcium fluoride or sodium chloride. Consequently, along with electron-transfer processes, hole transfer may also be important. Most transition

metals replace Ti^{4+} substitutionally in the lattice. Many strontium-titanate crystals that are singly or doubly doped with transition metals (for example, iron, cobalt, nickel, iron-molybdenum, cobalt-molybdenum, nickel-molybdenum) show photochromic effects. The iron and iron-molybdenum materials illustrate the general behavior. Figure 6a shows the absorption spectra of iron-doped strontium titanate induced by ultraviolet irradiation at different temperatures. Compared with the pure material, the band-edge absorption is broadened around 400 nm. When ultraviolet light of wavelength less than 450 nm is absorbed by the material, the crystal becomes dark; the broad absorption band of figure 6a is induced. This absorption can either be bleached out with light of wavelength greater than 450 nm or the material will clear thermally at a rate depending on temperature.

The photochromic mechanism for the singly doped strontium-titanate crystals is again aided by lattice defects. Most of the iron ions enter the lattice on Ti^{4+} sites and are charge compensated by oxygen vacancies. In the photochromic process an electron is transferred from the Fe^{3+} ion to the

lattice defect associated with the vacancy, converting Fe^{3+} into Fe^{4+} . The reduction of the number of Fe^{3+} ions present is observed during the coloration process by electron paramagnetic resonance (EPR) techniques. In the bleaching process the electron is returned to the Fe^{4+} ion via the conduction band by photoexcitation from the vacancy trap. Different configurations of the lattice defects associated with the oxygen vacancy can lead to different trap depths, causing a very broad inhomogeneous absorption band. This inhomogeneous absorption can be demonstrated by preferential bleaching of the induced band or by its very strong temperature dependence.

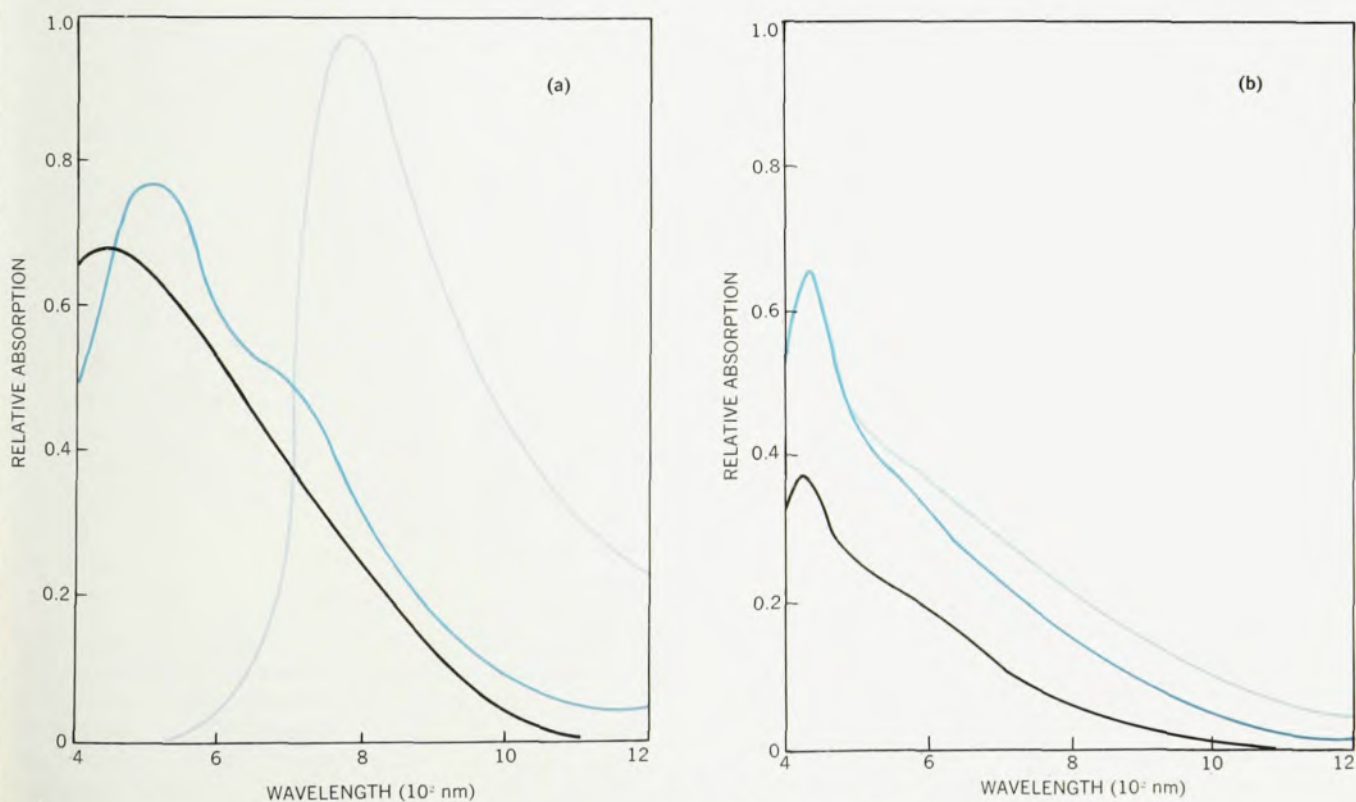
Doubly doped crystals

When in addition to the iron, molybdenum is also incorporated into the crystal, the induced absorption spectrum changes (as shown in figure 6b). The shape of the induced absorption bands is the same at different temperatures, and the thermal stability of the coloration is increased. All these phenomena can be explained by charge compensation of the Fe^{3+} ion, which can now take place by one Mo^{6+} substitution or a Ti^{4+} site for

each two Fe^{3+} ions, leading to a single trap depth associated with this Mo^{6+} ion. Initially the material is essentially colorless because neither Fe^{3+} nor Mo^{6+} absorb in the visible region of the spectrum. In the photochromic process an electron is transferred from Fe^{3+} to Mo^{6+} , changing the ions to Fe^{4+} and Mo^{5+} .

In the colored state the absorption comes from the Fe^{4+} ion and the Mo^{5+} ion. This valence change can be monitored by following the decreasing intensity of the cubic Fe^{3+} EPR signal and the corresponding increase in the Mo^{5+} EPR signal while the crystal is irradiated with ultraviolet light.¹⁰ The nature of the actual charge-transfer mechanism is not clear. It can either take place by the transfer of electrons through the conduction band, by the transfer of holes through the valence band or by some combination of the two processes, that is electron-hole pair excitation (figure 7).

Barium titanate and calcium titanate display similar phenomena. The induced optical absorptions are very similar, the main difference being in the thermal stability of the colored state. For example the thermal lifetime of the induced coloration in iron-doped calcium titanate, strontium ti-



TEMPERATURE DEPENDENCE of induced absorption spectrum of strontium titanate doped with (a) 0.01% iron and (b) 0.025% iron and 0.12% molybdenum. Measurements were made at 300 K (black), 77 K (dark color) and 4.2 K (light color).

—FIG. 6

tanate and barium titanate are about 10^2 , 1 and 10^{-2} seconds, respectively, at 300 K. The shape of the induced absorption bands changes drastically with different dopants.

Other inorganic materials

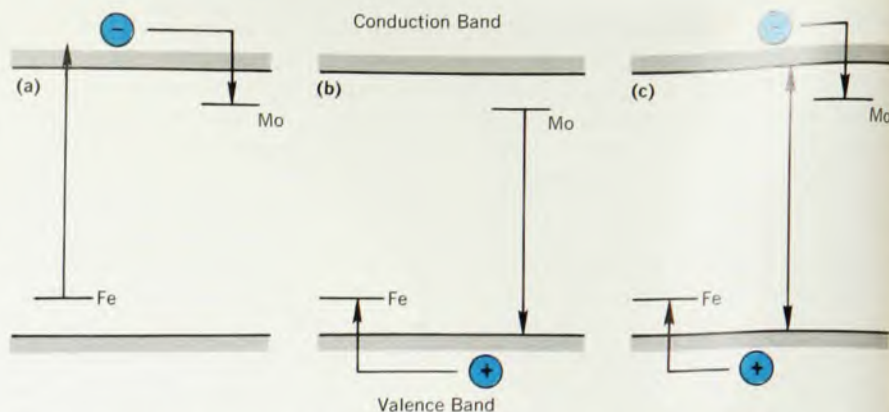
Robert K. Swank reported several strong absorption bands in X-irradiated Holophosphate crystals. At least three different types of anisotropic color centers are responsible for the color changes. The exact nature of the centers has not been established. These materials may be of interest from a practical point of view, because the "write" and "erase" bands are in the ultraviolet region of the spectrum, and there are several possible "nondestructive-read" absorption bands in the visible.

When rocks containing the mineral hackmanite ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot 2\text{NaCl}$) are broken, the freshly exposed surface is deep magenta, which fades rapidly in sunlight. Synthetic materials have also been prepared with similar photochromic properties. When the chlorine atom is replaced by a bromine or iodine atom, instead of the magenta color, violet and blue appear after irradiation with light of wavelength about 300 nm. The single broad absorption band around 500 nm that is responsible for the coloration again results from some color center.¹²

One commercial product now available that uses the photochromic process is photochromic sunglasses. For large-area application, glass media are highly attractive. The photochromic effect in glasses may be attributed to color centers,¹³ to impurity dopants such as cerium or europium, or to a process analogous to the photographic process using silver halides.

PHOTOCHROMIC PARAMETERS

A photochromic material could function as a light-sensitive medium that can be addressed, erased and interrogated by light. The sensitivity of the medium is the induced optical density change per unit of absorbed light energy, where the optical density change is the logarithm of the ratio of the transmitted light intensity to the incident intensity ($\log_{10} I/I_0$). Unlike photographic film, this is a photosensitive medium without gain. The upper limit on the sensitivity is set by the total absorption cross section of allowed transitions of the photochromic centers. For optimal performance,



MECHANISMS OF CHARGE TRANSFER in strontium titanate doped with iron and molybdenum, showing (a) electron, (b) hole and (c) electron-hole pair excitations. —FIG. 7

each photon absorbed induces one photochromic center. Such a material has a photochromic efficiency η of unity.

Sensitivity

We may estimate the sensitivity of an ideal material with unit photochromic efficiency by computing the energy necessary to achieve an optical density of unity. Because the intensity transmitted is a function of the depth x and the absorption coefficient σ , this value ($\log_{10} I/I_0 = 1$) specifies a given product $x\sigma$. Furthermore a version of Smakula's equation¹⁴ relates σ to the oscillator strength f

$$f = \frac{1.08 \times 10^{18}}{N} \frac{n}{(n^2 + 2)^2} \sigma_{\max} \Delta\nu_{1/2}$$

N is the number of centers/cm³, n is the refractive index and $\Delta\nu_{1/2}$ is the full width of the absorption band at half height in cm⁻¹.

Using this relationship and assuming $f = 1$, we may determine the number of centers and thus, from the assumption $\eta = 1$, the number of photons incident per unit area. For a visible absorption band with half width $\Delta\nu_{1/2} = 3000$ cm⁻¹, the energy absorbed is 5×10^{-3} joules/cm² for our ideal material. Presently existing calcium-fluoride and strontium-titanate materials require light energies of about 5×10^{-2} joules/cm², or a factor of ten higher, to obtain an optical density of unity.

Transition rates

There are really three different transition rates that relate to photochromic phenomena. The first is the rate of electron transfer, for example, in the

mechanism in calcium fluoride or strontium titanate. This rate, which can be faster than 10^9 sec⁻¹, depends on the absorption cross section of the charge-transfer band, the mobility of the electron in the conduction band and the capture cross section of the trapping impurity. Experiments measuring the time dependence of the absorption change under illumination by a Q-switched ruby laser¹⁵ verify that the rate is greater than 10^7 sec⁻¹.

Thus the second rate of interest is the rate at which light energy may be delivered to the sample. In most instances the sensitivity of the material, that is the available light intensity, rather than the photochromic mechanism, will be the limiting factor in the switching rate.

Finally, the lifetime of the induced absorption band is important. For an electronic trap the thermal stability depends on the trap depth and the temperature. Thermal lifetimes (the time to decay to half the original absorption intensity) ranging for 10^{-3} seconds to months have been observed at 300 K. The time dependence of the decay can have a complex form, characteristic of several center-decay processes.

Resolution

The "grains" limiting the resolution of the photochromic material are the atomic centers themselves, or the separation between them. In practice the resolution will be limited by the diffraction limit of the addressing light beam. Three-dimensional holograms made from photochromics demonstrate this resolution.

Several display and information-storage applications require that the visible photochromic change (optical density of about 0.5) take place in a material thickness comparable to the resolution standards, about 1-micron thickness. Whereas there are some organic films in which this requirement can be almost satisfied, inorganic materials have a maximal optical density change of 30/cm, requiring at least 150-micron thickness to obtain an optical density of 0.5. To remedy this situation, the concentration of photochromic centers must be increased. In the best photochromic material, strontium titanate doped with iron and molybdenum, the concentration of active photochromic centers is approximately $10^{18}/\text{cm}^3$; one out of every 10^4 titanium ions is replaced by an active center. To increase further the number of active centers is a difficult task.

DIRECTIONS AND APPLICATIONS

Several inorganic photochromic materials have useful applications but many problems remain to be solved. They are:

- calculation of the energy states of isolated impurities in the bandgap of insulators
- formulation of the nature and intensity of charge-transfer spectra and charge-transfer mechanism
- determination of the mechanism of nonlocalized electrical charge compensation of impurities
- reduction of the limitations on the photochromic concentration
- growth of crystals in large-area high-quality formats

Several photochromic effects might be exploited. One is the refractive index caused by the light-induced anomalous dispersion, which could be used to store phase-holograms and their nondissipative readout. Another is the field of "cathodo-chromism," or the inducement of color change by

electron-beam bombardment instead of ultraviolet irradiation. Finally, the combined effects of light and electric field on the ionization of the traps could be explored.

Among the several possible applications are three likely areas where photochromics can be used—computers, optical information storage, and processing and display systems.

Use in computers

Computers demand increasingly larger memory capacities. Present-day computers can store in their magnetic-core memories up to 10^7 bits of binary information. *In principle* if one could utilize the resolution capabilities of photochromic materials, 10^7 bits/cm² would require 3-micron $\times$ 3-micron resolution elements, well within the capabilities of diffraction-limited laser optics. Moreover each of these channels has a "gray-scale capability," that is, several binary bits per channel could be accommodated, leading to about 10^8 bits/cm² capacity. To introduce redundancy, the information might be stored in a hologram form. While this large storage capacity exists, at present it is not clear just how this optical memory could best be coupled to existing systems. For large auxiliary permanent memories, photographic films can be used. An erasable version of this photographic film memory that could be updated might be the first step in using photochromics.

As a real-time working memory, the sensitivity of the material places limitations on the speed. For an ideal material, every time the content of 1 cm² would be written or erased, 5×10^{-3} joules of light energy would have to be dissipated. If we assume that 50 watts of heat can be carried away from the 1 cm² surface area, the whole content (about 10^8 bits/cm²) can be changed 10^4 times each second. Of course to "read only" requires much less light, and there the material

would not limit the speed. Moreover each "erase" or "write" operation could be very fast (for example, 10^{-8} seconds to put in a hologram with a Q-switched laser pulse).

At this point it is impossible to predict in what format photochromics will be used in computers, but the parameters of resolution, sensitivity and speed strongly indicate a useful function. There are also other possible recording media, such as thermoplastics and magnetic films, against which photochromics will have to compete. The success of photochromics will depend on our ability to increase the concentration and to find a material with a thermally stable photochromic lifetime of several years.

Optical processing

In coherent optical processors, photochromic materials could be used as the continuously changeable image plane or reference plane. Photochromic tapes could take the place of erasable magnetic tapes with about a 100-fold increase in the information capacity. Sheets of photochromic papers might provide a soft copy (reusable) form of printout. In storage systems such as microfilm, an updatable format (for example, a list of insurance policies or a list of parts) could use photochromics.

Display systems

In display systems a photochromic film could be used in projection. Photochromic powder replacing the phosphor in a cathode-ray tube can be used as a reflective "cathodochromic" storage tube.¹⁶ A most intriguing possibility exists for a three-dimensional television display. Where a hologram would be received by the set, the electron beam would reproduce the hologram on the photochromic film face of the television tube, and this hologram then could be viewed in a coherent light to reproduce the three-dimensional image.

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