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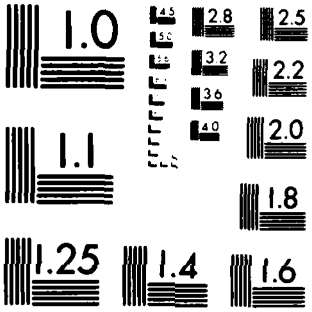
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SAFETY EYE PROTECTION THROUGH USE OF FAST ACTING OPTICAL SWITCHING

January 1984

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The Pennsylvania State University
Materials Research Laboratory
University Park, Pennsylvania 16802

FINAL REPORT

Contract No. DAAG46-82-K-0056

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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Due to the increasing use of lasers in military applications, along with their high power levels and short pulse times, there is a critical need for fast acting optical switches to protect the vision of personnel. Such devices must be economical, suitable for use either in optical components (eg. binoculars and windshields) or in eye glasses or goggles, be responsive to laser energies from the UV to the near IR, and not impare the performance of the personnel in their mission. At present there are no materials/systems

which fulfill these requirements. As a first step in developing new materials and materials related devices which are capable of switching from optical densities of less than 1 to greater than about 5 in times of a microsecond or less a critical review was undertaken. The main findings of this study are that there are four materials types which have potential for improved fast acting optical switches: (1) ferroelectric liquid crystals; (2) organometallic films containing charge transfer complexes, which undergo field-induced redox reaction, (3) inorganic electrochromic films which undergo insulator-semiconductor or insulator-metal transitions due to short range diffusion; and(4) inhomogeneous media in which the inhomegeneity is on the order of the wavelength of visible light. At present there are not obvious ideal solutions based simply upon known optical properties of materials. For improvements beyond those suggested above it may well require new discoveries (eg. nonlinear optical phenomena) or more sophisticated, engineered optical systems (eg. based on holography, diffraction, and interference effects).

ABSTRACT

Due to the increasing use of lasers in military applications, along with their high power levels and short pulse times, there is a critical need for fast acting optical switches to protect the vision of personnel. Such devices must be economical, suitable for use either in optical components (eg. binoculars and windshields) or in eye glasses or goggles, be responsive to laser energies from the UV to the near IR, and not impair the performance of the personnel in their mission. At present there are no materials/systems which fulfill these requirements. As a first step in developing new materials and materials related devices which are capable of switching from optical densities of less than 1 to greater than about 5 in times of a microsecond or less a critical review was undertaken. The main findings of this study are that there are four materials types which have potential for improved fast acting optical switches: (1) ferroelectric liquid crystals; (2) organometallic films containing charge transfer complexes, which undergo field-induced redox reaction, (3) inorganic electrochromic films which undergo insulator-semiconductor or insulator-metal transitions due to short range diffusion; and (4) inhomogeneous media in which the inhomegeneity is on the order of the wavelength of visible light. At present there are no obvious ideal solutions based simply upon known optical properties of materials. For improvements beyond those suggested above it may well require new discoveries (eg. nonlinear optical phenomena) or more sophisticated, engineered optical systems (eg. based on holography, diffraction, and interference effects).

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I. INTRODUCTION

Lasers operating in the visible portion of the electromagnetic energy spectrum present a serious safety hazard for personnel either directly observing or using optical systems. Presently there are many lasers being used by the military. They are used as rangefinders, target locators and designators, and projectile simulators for training purposes. In the future directed energy weapons are expected to be practical.(1) The most common lasers being used include: pulsed neodymium:YAG (1064nm), gallium arsenide diode (850 to 905nm), pulsed ruby (694.3nm), helium-neon (632.8nm) and doubled Nd:YAG (532nm). In the near future iodine (1315nm) and argon (351nm) lasers may also be part of the field inventory. And just beyond that lie high-power, tunable excimer, dye, and free-electron lasers operating over a wide range of visible and ultraviolet wavelengths.

The Nd:YAG and gallium asenide diode lasers both operate in the near infrared (IR) beyond the visible region of the spectrum but at wavelengths which are still transmitted well by the optics of the eye and absorbed at the sensory retina. The retina absorbs about 50% of the visible, and a slightly lower percentage of IR, radiation entering the pupil. Energy densities of 0.004 J/cm^2 on the retinal image area in 150 msec (the eye-blink response time) will cause flash blinding, while levels greater than that can cause permanent lesions. Thus optical switches that can be triggered by these light levels and photon energies and can respond in times much less than the eye-blink response time are desired.

The use of filters or dyes for protections against specific wavelengths is often an acceptable solution, but the problem with filtering against many different wavelengths simultaneously is that the optical density (O.D.) becomes too great and mission effectiveness is severely hampered. In addition, interference filters tend to be ineffective at large angles of incidence and this effect is further enhanced when several filters are stacked.

In order to protect against multiple wavelengths, essentially all optical and near IR wavelengths, it appears that what will be required is an optical shutter which goes from a highly transmitting state to a non-transmitting state in times sufficiently small to ensure eye protection. Fast acting optical switches based upon PLZT ceramics have been developed to protect personnel against the bright flash from nuclear explosions. The switches are used in goggles that operate in $\sim$1 msec (O.D. 1 to O.D. 4.6). However PLZT goggles are too expensive to supply in large numbers and have too slow of a response time for anticipated laser energies. An inexpensive optical switch that can function in at least the microsecond range (the faster the better) is needed. An O.D. of 1.0 prior to switching is acceptable and an O.D. of 4 to 6 after switching is required to provide protection.

II. OBJECTIVES

Therefore, what is required are new optical switching materials or materials-based systems which have the combination of high speed, large decrease in transmission in an on-state, high optical transmission in the off-state, ease of operation, and economic feasibility. It would be preferred that the optical switching process be both reversible and operate in a transmissive mode but depending upon cost, convenience, and switching properties an irreversible and/or reflective mode switching process might be practical.

Optical switching effects (eg. electro-optic effect, magneto-optic effect, dynamic scattering in liquid crystals) in single phase materials have been known for years. However, a comparison of these effects, especially as they relate to the present application of eye protection, has not been made. Furthermore, hybrid materials (eg. multiphase or composite materials) or hybrid materials-based systems (eg. multilayer structures) have been studied even less in regard to optical switching, and yet they open up an even wider avenue to possible solutions.

What is needed is an exploratory study of all materials properties as they related to fast optical switching processes and to search the literature for current developments in new materials. It is expected that most practical fast optical switching devices will contain not only an optically active material (capable of bistable switching in some manner) but also other materials for sensing the laser beam (primary effect) and for applying a secondary effect (eg. current, electric field, temperature gradient). Although the primary emphasis will be on the optically active materials, some attention will be given to other materials that might be used in an overall system and the speed with which they can respond. Potential and typical optical switching device structures will be discussed, but again there will be no attempt at completeness. As will be shown, it will most likely be the bistable switching process of the optically active material which is the overall rate limiting mechanism in any device structure.

Thus a general classification and comparison of all optically active materials will be carried out. From this broad analysis several materials/processes will be selected as showing presently the greatest potential for fast and practical optical switches. Future research areas for each of these materials will be suggested. Finally an overall assessment of optical switching processes for achieving an ideal solution to the problem at hand will be given.

III. APPROACH

In general optical switching results from the movement or rotation of structural units under an externally generated force such as electric field or magnetic field or heat. In many cases the structural unit is anisotropic and the applied force tends to align these units in a preferred direction. Such a structural switch results in property changes such as the refractive index in the direction of the incident light (eg. uniaxial ferroelectrics) or increased scattering (eg. nemetic liquid crystals) and leads to alterations in the phase and amplitude of the transmitted light. In other instances where either charge-transfer or phase-transformation processes occur, there can be large changes in the band structure or surface morphology leading to increases in either absorption or reflection of the incident laser light.

The fundamental structural unit controlling optical switching processes varies from the atomic scale (eg. charge transfer absorption and color center formation), to the nanometer-scale (eg. submicron colloidal dispersions and liquid crystals), to the micrometer-scale (eg. composite structures with dimensions close to the wavelength of light), and all the way to the macro-scale (eg., crystallization processes). This then offers another way to classify these materials. To a certain degree the speed of switching is going to be inversely related to the size of the transforming unit. However, the matrix in which the unit exists is just as important since it defines the constraining forces on the units. For instance, liquid crystals and their domain structures exist in a very fluid medium compared to inorganic ferroelectric crystal domains.

In the next section we will structure our optical switching materials classification scheme by starting with the primary laser beam and initially consider the three general ways in which it can be altered - transmission (rotation, retardation, and scattering), absorption, and reflection. Each of these general optical processes will then be subdivided according to the secondary effect which drives the optical switch. Within these subcategories we will discuss the different optical processes which have potential for fast optical switching along with the various classes of materials and specific materials for each.

IV. TECHNICAL DISCUSSION

A. Laser Energies Anticipated

Lasers are high energy sources of highly collimated and monochromatic radiation. Currently fielded lasers include the pulsed Nd:YAG (1064nm) laser used as a target locator/designator by ground troops and the Q-switched ruby (694nm) laser used as a range finder on tanks. In both cases the lasers are typically operated at 100mJ/pulse and the pulse width is between 10 to 30nsec. Beam divergence is typically 0.25mrad and beam diameter at the laser exit port is about 2cm. Under these conditions the total introcular energy collected under typical viewing conditions have been calculated as a function of distance from the laser source.(2) (See Figure 1).

The horizontal lines in Figure 1 represent three critical energy levels at the sensory retina for the two lasers considered. The lines for vitreal hemorrhage and retinal burn (energy at which an opthalmoscopically visible lesion is produced) are based upon tests on rheusus monkey eyes and represent the dose at which the effect is obtained 50% of the time (ED_{50}). The lower lines represent the maximum permissible exposure (MPE) and is somewhat arbitrarily chosen using the rule of thumb of dividing the ED_{50} level for retinal burn by a factor of 10 to 100, the exact factor depending on the wavelength range and exposure conditions.

The main point is that at typical tactical distances, 0.1 to 10km, there is a significant chance for temporary or permanent blindness if a person directly views the laser radiation. Furthermore, at these distances the beam does not decrease in energy density enough to be harmless but it does increase in total area enough to have a significant chance of intercepting one, and probably both, eyes of anyone looking toward the laser. For instance, a 2cm diameter beam at a distance of 1km would cover an area of 25cm diameter to 1m diameter for 0.25mrad and 1.0mrad divergence angles, respectively, in a non-scattering, non-turbulent atmosphere

These lasers are not even intended as weapons. As more powerful lasers are developed the protection of personnel against their ocular hazards will become more important and more difficult. From Figure 1 it can be seen that the energy level of a typical current laser as viewed at 1km must be attenuated by a factor of from as small as 10^1(O.D.1) (for a 3mm pupil viewing a Nd:YAG laser) to as large as 10^4 (O.D.4) (for viewing a ruby laser through M-17 binoculars). And of course smaller distances would require larger O.D. changes. Since these calculations have been for laser pulses of only 10^{-8}sec duration, it is now seen that an effective optical switch has very stringent requirements. Furthermore, much higher power lasers are expected in the future.

switch has very stringent requirements. Furthermore, much higher power lasers are expected in the future.

B. Energy Balance

One manner in which to classify optical switching processes is to consider the total energy balance of the system. When a laser beam impinges any surface, such as an optical switching device, it is essentially a linearly polarized, monochromatic light beam with a given amplitude and phase. The phase angle in the plane perpendicular to the beam direction is generally unknown.

There are three general processes which occur: the laser beam can be transmitted, absorbed, or reflected. Since the object is to produce bistable switching with a reasonably high transmission in the on-state (O.D. ≤ 1), at least one state of the device must have low total absorption and reflection losses. In order to switch to an off-state with very low transmission (O.D. > 4), the state of the transmitted, absorbed, or reflected light must be switched rapidly.

Switching can be achieved by altering the state of the transmitted light by one of three ways: optical rotation of the direction of the plane polarized light, optical phase retardation of the direction of the plane polarized light, and optical scattering of the beam in directions away from the optical path of the viewing geometry. Since the rotation or retardation of plane polarized light by itself has no change in terms of the total energy transmitted, the only practical schemes for optical shuttering include two crossed polarizers. If the plane of polarization is rotated through 90°, either through true optical rotation or half-wave retardation, then switching between two states where the polarizers are either optically aligned or crossed is obtained. A general device configuration is shown in Figure 2(a). The optical transmission in the on- and off-states are then controlled by the characteristics of the polarizers and the switching speed by the physical process leading to 90° rotation of the plane of polarization. The laser beam energy is absorbed by the polarizers, generally to an O.D.$\sim$4.5, and thus damage thresholds must be considered when selecting polarizers. One possible optical switch based on phase retardation of the incident light will have a maximum contrast ratio (T_{ON}/T_{OFF}) when half-wave retardation (effectively

90° rotation of the plane of linearly polarized light) is obtained. Polar dielectric materials with a high birefringence and the ability to switch the polar axis by 90° will give this condition. The transmission is given by$^{(3)}$

$$T = (1-A-R)(\sin^2 2\theta)(\sin^2 \frac{\pi \Delta n\, t}{\lambda})\, T_p$$

Where A is the absorption in the dielectric, R is the reflectance from the dielectric surface, θ is the angle between the polar axis of the dielectric and the polarizer axis, Δn is the material birefringence, t is the thickness of the material, λ is the wavelength of the incident light, and T_p is the transmission of the two polarizers. The maximum transmission is achieved when the polar axis of the dielectric is perpendicular to the optical axis and at 45° with respect to the two crossed polarizers [see Figure 2(b)]. Under this condition $T_{on} \approx T_p$ ($\parallel$) when A and R are small and $\Delta n\, t$ ($=\Gamma$, retardation) is $N\lambda/2$ ($N = 1, 3, 5 \ldots$). The minimum transmission is obtained when the polar direction of the dielectric is parallel to the optical path at which condition there is zero phase retardation. For this second state the light is directly transmitted by the dielectric and thus light is blocked to the extent of the crossed-polarizer efficiency [$T_{OFF} \approx T_p(\perp)$]. The contrast ratio, therefore, is essentially that of the polarizers (∼30,000:1). A discussion of materials that can achieve such conditions, as well as other device configurations based on optical rotation and retardation will be given later. At this point it is seen that the higher the birefringence of the material, the lower will be the thickness required. Also the ability and ease of switching the polar axis by 90° will be an important consideration.

Natural optical activity (or the rotation of the plane of polarization of light as it passes through the medium) occurs in many materials for a variety of reasons: (i) in the liquid-state or solutions, the molecules may be intrinsically asymmetric (i.e., it does not have a mirror or a center of symmetry) or the conformation long chain molecules may be in a helical shape, (ii) in the cholesteric liquid crystal state the molecules may be arranged in a helical configuration and (iii) in the crystalline state the atomic arrangement is such that the crystal lacks center of symmetry; and mirror plane symmetry, if present, does not exclude optical activity in certain directions. The optical activity is wavelength dependent and varies quite strongly as we approach the characteristic absorption wavelength.

By external perturbations, such as temperature variation or application of pressure, one can vary the magnitude of optical activity and thus this approach can be used to effect a 90° rotation of the plane of polarization of light and thus act as an effective reversible switch. But of the three groups mentioned above only the liquid crystals are obvious candidates for this approach since the optical activity as well as their variation with temperature or pressure are rather very small for the other two groups of materials as compared to the liquid crystal.

Light scattering processes do not require polarizers but rather depolarize the directed incident light and scatter it in all directions [see Figure 2(c)]. In order to minimize the light transmitted in the off-state the numerical aperture, which defines the cone of light transmitted along the optical path of the system, must be small.(3) This in turn limits the transmission in the on-state to values of 20% of less. In scattering processes there is always a trade-off between increasing the scattering angle (numerical aperture) and increasing the contrast ratio. For large numerical apertures such as needed for eye glasses, contrast ratios of only 10 to 1 are likely (Δ O.D. = 1). For large overall contrast ratios at least four scattering layers would have to be placed in series (cascading). Because scattering is fairly independent of the angle of the incident light, they maintain a fairly constant contrast ratio at wide viewing angles. Since the light is not absorbed in the active scattering medium but scattering into a larger surrounding volume, heating should not be a problem.

Scattering of optical wavelengths requires inhomogeneous media in which the optical properties of adjoining regions are significantly different and the inhomogeneous regions have dimensions on the order of, or greater than, the wavelength of light. Such conditions exist in ferroelectrics with a large, random domain structure and in liquid crystals where the sub-μm sized molecular. cigar-shaped molecules coalesce to form clusters with sizes greater than a μm. For both classes of materials switching from non-scattering to scattering structures can occur.

The second general process for optical switching involves a rapid change in the optical absorption of a material. Much higher on-state transmission is possible since the active material itself is the absorber and there is no need for polarizers. However, that also means that the optically absorbing material must be able to deal with the absorbed thermal energy. The optical density equation can be derived from the Beer-Lambert Law and is defined as,

$$\text{O.D.} = \log_{10} \frac{I_o}{I} = 0.43\alpha t$$

where α is the absorption coefficient in cm^{-1} and t is the material thickness in cm.

Ways in which absorbing centers can be created in an initially transparent material include: (1) defect generation; (2) charge-transfer processes; (3) phase transitions (both first and second order); (4) reorientation of dichroic dye molecules; and (5) large fluctuations in optical density with sizes on the order of the wavelength of light. Again, for practical switching devices the absorption center formation must have a low activation energy for the transformation process (directly related to switching speed) and result in a large $\Delta\alpha$ for reasonably thin materials. Of the methods above the defect generation and first order phase transition processes can be eliminated due to low $\Delta\alpha$ and low speed, respectively. The remaining processes will be described later.

Reflection is the third general process for devising an optical switch. And although it is the preferred method, it also presents the most difficulty. In a reflection process, if perfect, the laser energy is not absorbed and this then eliminates any heating problems. What is required is a fast insulator-metal transition in a material or the rapid deposition of a free-electron metal as initiated by the laser beam at a gas/solid or liquid/solid interface. The latter process seems to be possible since deposition rates of 10^8Å/sec would be needed for coating a 100Å film in 1 usec, while rates recently reported(4) are already as high as $\sim 10^6$Å/sec for Au. Insulator-metal transitions have been reported for a wide range of mechanisms including amorphous-crystalline transition, crystalline phase transitions, narrow d-band transitions, and high pressure. Although no practical fast optical switches have been reported using these processes, several at least hold some potential.

C. Secondary Effects

As just described there are a variety of approaches to designing a fast optical switch. In all cases considered in this study there is a material which undergoes some type of transition as the result of a driving force. The primary driving force, of course, is the incident laser beam but in most instances the switching transition is driven by some other indirect force or combination of forces. In this section the three general transformation processes will be subdivided according to these secondary driving forces. For the few cases where more than one secondary effect is occuring, they are classified according to the main effect.

Using the classification scheme just described, the various optical processes/materials which at present appear to have potential for fast switching speeds (on the order of microseconds) and large ΔO.D. (1→5) in a practical transmissive device are listed in Table 1. Although there is a much larger number of possible optical switching processes, those processes which are too slow (eg. electrochromism due to long range proton diffusion, first order phase transitions) or too small of an effect (eg. Stark effect, Franz-Keldish effect, photo-refractive effect, color center formation), or too impractical for bistable device operation (eg. many thermo-optic effects, elasto-optic effects), will not be discussed any further.

There are several important observations to be made about Table 1:

1. Most of the fast optical switching processes are based on electro-optic properties of materials. There appear to be three reasons for this: first, an electric field has a relatively large effect on polar materials; second, electric fields can have very fast response times, even for indirect processes such as photoconductors or photovoltaics which sense the laser beam and trigger a fast acting electronic circuit; and third, voltages can be controlled accurately for bistable operations.

2. The two most important classes of materials are the ferroelectrics and liquid crystals. This follows directly from 1) since it is these materials which would be expected to have the greatest interaction with an electric field. Although the ferroelectric materials based on electro-optic phase-retardation have been more highly developed and currently are the fastest optical shutters made [50 μsec(5) with potential for 1-10 μsec(3)], the liquid crystal materials seem to have potential(6) for being faster and more pratical.
3. Even though no practical optical switching devices have yet been discovered based on nonlinear optic or electro-optic effects, the possibility for large and fast optical switching effects exists. For instance, it has been recently reported(7) that anomalously high switching speeds occur in organic polymer ferroelectric films under intense electric field such as those created by an intense laser beam.

Before discussing each of the potential fast optical switching processes/materials/devices indicated in Table 1, it will be useful to consider some limitations on the ultimate speeds with which the different materials can be optically switched.

D. Switching Speeds

There are a variety of different switching processes which are included in Table 1. In a general sense these can be grouped into: (1) those requiring a reorientation of an anisotropic unit (structural, dielectric, and magnetic anisotropy) under the influence of a driving force such as electric field, magnetic field, heat, and internal structural constraining forces; (2) electronic charge transfer; (3) short range diffusion; and (4) rapid crystallization.

Dielectric relaxation studies are extensively used for determining the orientational dependence of the polarizability in polar molecules in liquids and polar solids. The simplest case of liquids with freely rotating spherical polar units has been considered by Debye.(8) From basic friction, viscosity, Brownian diffusion and thermal energy considerations, a relaxation time, τ, is obtained

$$\tau \approx \frac{4\pi a^3 \eta}{kT}$$

where a is the radius of the spherical unit (eg. molecule) and η is the viscosity of the medium. For water ($a \approx 10^{-8}$ cm, $\eta = 0.01$ poise) the relaxation time is approximately 10^{-11}sec. A low viscosity liquid crystal ($a = 10^{-6}$cm, $\eta = 0.1$ poise) would have $\tau \sim 10^{-8}$sec if the frictional drag of the nonspherical molecules and the interaction between closely spaced chain molecules were ignored. This is comparable to the experimental value of 10^{-10}sec dielectric relaxation time for the common liquid crystal PAA.(9) The rotational diffusion constant for flexible chain molecules has been considered by Kirkwood and Riseman,(10) Isihara,(11) and Jernigan and Thompson.(12) In these studies both the frictional coefficients of the longer molecules as well as the hydrodynamic interaction of the molecules have been considered. The later authors have shown that for a low viscosity medium with a flexible polymer immersed that relaxation times varied from 10^{-8}sec for low molecular weight polymers (10^4) and 10^{-5}sec for larger molecular weights (10^6).

As the molecules become larger and the viscosity increases, the relaxation times increase. For solids there is a much more rigid barrier to internal motion because of stronger bonding and the relaxation times are usually much longer as compared to liquids. It is more difficult to take into account effects such as the applied field on orientation energy, induced dipole moments in strong fields, and cooperative effects among polar molecules moving in unison.(7) Thus the numbers just given are only lower estimates and experimental evidence must be relied on in many instances to give actual limits. At present, switching speeds in both organic(7) and inorganic(13) ferroelectrics have been reported in the 1-10μsec range while recently sub-μsec switching in ferroelectric liquid crystals has been demonstrated.(14) And switching speeds in ferrimagnetic materials have been shown as low as 1μsec resulting from magnetic domain wall movement speeds as high as 900m/sec.(15)

Of the three classes of materials, the liquid crystals appear to have the greatest potential for further improvements in speeds due to the latitude the materials designer has in altering the properties of liquid crystals. This coupled with relatively low cost, low power for operation, and high optical response make liquid crystal light values an important area for study

The speed with which electrons can be transferred in charge-transfer complexes is expected to be quite fast. Electronic and optical switching speeds of 5nsec have been found in semiconducting organometallic films.(16)

Short range diffusion under the influence of intense electric fields and rapid thermal gradients is generally unknown. It is difficult to measure chemistry changes over the 2-10Å range unless some large property change in the material occurs. From recent laser annealing studies(17) it seems that in principle atomic movement over those small distances can occur in μsec times. If such effects were found to occur in electrochromics which normally rely on diffusion over thousands of angstroms, then rapid switching electrochromics would be possible, since the second step of the electrochromic process is charge transfer which is not a limiting process.

Rapid crystallization processes due to intense laser heating have been shown to have speeds on the order of 1-10m/sec.(18) Since the materials in which such an irreversible process might have application involve insulator-metal transitions, a film thickness of only several hundred angstroms ($\sim 10^{-8}$m) needs to be crystallized before nearly complete reflection due to the metallic state is achieved. Thus switching times in the nsec-range would seem possible.

E. Materials, Processes, and Devices

Nearly all of the practical optical switching processes which alter the state of the transmitted light by either rotation, retardation, and scattering, rely on the interaction of either an electric field or heat with a polar dielectric material. The optical switching effect occurs by altering the average polar direction state of the material in any one of a number of possible ways. Since both ferroelectrics and liquid crystals contain highly polar units which have a large and useful effect on optical properties, a considerable amount of literature exists on both of these important classes of polar dielectrics covering everything fron theory to complicated devices. No attempt is made to cover these two areas completely. Rather, a general discussion is given along with the most promising directions for obtaining fast optical switches. A number of books and review articles on ferroelectric(3,19,20) and liquid crystal(21-27) materials and devices have been published, and can be referred to for details.

There are two electro-optic effects in polar dielectrics that affect the phase retardation: the linear Pockels effect ($\Delta n \sim \vec{E}$) and the quadratic Kerr effect ($\Delta n \sim \vec{E}^2$). For ferroelectrics the linear electro-optic effect has the largest effect for polar materials with high coercive fields while the quadratic electro-optic effect is found in nearly cubic phase materials which are close to a ferroelectric phase. A listing and comparison of linear and quadratic electro-optic coefficients is given by Burfoot and Taylor.(3) For a pratical switching device there are two possible modes of operation: changes in Δn due to partial switching along the polar axis [Figure 3(a) and (b)] and changes in Δn due to switching of the polar axis direction [Figure 3(c)]

Large area devices based upon ferroelectric single crystals are not practical from an economic point of view. With the discovery of transparent ferroelectric ceramics by modifying lead zirconate-titanate with lathanum (PLZT), it was possible to devise practical devices.(28,29) This material is a nearly cubic phase and has a large enough quadratic electro-optic coefficient that half-wave retardation (condition for maximum transmission between crossed polarizers) is practical in a reasonably thin device. The Δn-partial-switching mode has been most extensively developed for light shutter applications with two different device configurations studied. The strain-biasing mode [Figure 3(b)] developed by Maldonadoet al.(30) has the advantage of longitudinal biasing mode (no need for interdigital electrodes) but the switching would obviously be affected by any external strains on the material. The transverse switching mode in fine-grained PLZT ceramics [Figure 3(a)] originally discovered by Land and Thacher(28) has been the mode used for development at Sandia Laboratories of PLZT flashblindness-prevention goggles (EEU-2/P) for the Air Force. A number of papers outlining the development of this material and optical switching device are given in References 31-39. Various aspects of this development program (eg. polarizer development, portable power supplies, fabrication techniques) will be important to any future development of a new material.

Another electro-optic effect in ferroelectrics is to introduce scattering centers into coarse-grained, ferroelectric PLZT ceramics(28) by switching from a near zero average remnant polarization state (maximum optical transmission) to a large average remnant polarization state (minimum optical transmision). The scattering occurs at domain boundaries and thus the effect is highly dependent on domain size relative to the wavelength of light, orientation of optic axis, and strains at the domain boundaries.(40) Such devices can have ultimate switching speeds about as fast as that for the Δn-partial-switching mode(3) ($\sim 10\mu sec$) and require no polarizers. However, the contrast ratio is low (cascading required) and the numerical aperture is low, both of which limit their usefulness in currently conceived devices.

The other major class of polar dielectrics - liquid crystals - have an even broader range of optical switching devices then ferroelectrics. Liquid crystals, as the name implies, have the properties of both liquids and crystalline solids. As a liquid they flow and fill a container and yet they also exhibit anisotropic physical and optical properties usually associated only with solid materials. The reason for their anisotropy stems from the fact that liquid crystals consist of rather long cigar-shaped molecules and that long-range orientational ordering of these aniotropic molecules exists. Furthermore, because of cooperative effects between the molecules, their electro-optical and thermo-optical behavior are completely different than either solids or liquids and require much smaller energies for the molecular rearrangement (and, therefore, changes in optical properties).

Liquid crystals, or mesophases, display three general types of molecular arrangements and are termed nematics, cholesterics and smectics (see Figure 4). The nematic mesophase [Figure 4(a)] consists of the rods all pointing in the same direction but in no particular ordered fashion. They have the lowest symmetry and show a positive dielectric anisotropy (i.e., long axis of molecules are in direction of the field). The smectic mesophase [Figure 4(c)] is similar to the nematics except there is an additional layer symmetry. They are also birefringent and have a positive dielectric anisotropy. Cholesteric mesophases are much different and consist essentially of nematically ordered layers in which the layers undergo a twist much like a stack of cards with each card rotated a fixed angle with respect to the preceding layer. The distance between layers that undergo a 360° twist is called the pitch. Cholesterics display both positive and negative dielectric anisotropy and are the most optically active of the three. Liquid crystals with nematic order can be changed to cholesteric order by the addition of an optically active (chiral) material, such as a cholesterol derivative.

In addition to these three general types of ordering, there are nine distinct polytypes of the smectics, and classified by the letters A to I. Also, there are a number of order variations depending on the wall effects and temperature. If the temperature is too high, the liquid crystal undergoes a transition into an isotropic phase much like a ferroelectric-paraelectric transition. In the isotropic phase the rod-shaped molecules are randomly oriented. This wide range of possible ordered structures is a direct result of a very delicate balance of the weak inter-molecular forces in liquid crystals. Thus just small changes in external forces, such as small temperature variations and weak electric fields, effect large changes in the molecular order and macroscopic properties. In particular the large structural anisotropy directly leads to large optical anisotropies such as birefringence ($\Delta n \approx 0.05$ to 0.20), optical rotation, absorption, reflection, scattering and color.

As a result of this combination of high degree of structural variability, large electro-optical responses, and low power levels, a number of potential devices have been conceived using liquid crystals. Over 10,000 liquid crystals, most synthesized and all organics, are now known whereas only a handful existed 15 years ago. Because of their commercial importance in the broad area of display technology, a considerable effort is expended each year in both developing new liquid crystals and improving their properties such as temperature range, chemical stability, optical activity, viscosity, and degree of molecular alignment.

Despite the fact that theoretical and experimental values for the dielectric relaxation times in liquid crystals (for reorientation of molecular dipole moments around the long axis of the molecules) are in the sub-nsec range,(9) until very recently the actual orientational switching speeds for effecting a large change in optical properties (ie., 90° rotation) were in the msec range. Although there are no commercial devices yet available for μsec switching times, within the last three years there have been several significant developments in that direction.

The possibility of the existence for spontaneous polarization ($\vec{P}$) in liquid crystals had been suspected for a long time but it wasn't until 1975 that Meyer et al.(14) discovered ferroelectric liquid crystals with the smectic C and H mesophases by measuring their linear field effect on the modulated orientation structure. Further studies(42-47) confirmed the ferroelectric properties of liquid crystals. Because of strong electric field coupling due to $\vec{P}\cdot\vec{E}$ torques, high switching speeds might be expected. Although initial switching times of 10^{-3} - 10^{-4}sec were reported,(46) Clark and Lagerwall(48) showed that by proper control of surface interactions they were able to increase switching times to less than 10^{-6}sec. The reason for this increase in switching speed was that the surface interactions suppressed the macroscopic antiferroelectric behavior of the ferroelectric smectic C due to a spiraling of the nematic director, $\hat{n}$, and thus $\vec{P}$. The spiraling occurs since the direction of $\vec{P}$ and $\hat{n}$ are perpendicular.

The main ferroelectric smectic liquid crystal studied to date is the smectic C phase DOBAMBC (P-decycloxy-benzylidene-P'-amino 2-methyl butyl cinnanate), though others are being investiaged.(49,50) Improvements in the preparation of uniform and stable DOBAMBC materials have recently been reported,(51) and more studies and improvements are expected in the near future due to their technological potential.(52)

Clark and Lagerwall demonstrated that by eliminating the $\hat{n}$ and $\vec{P}$ spiral around the direction normal to an applied electric field $\vec{E}$ through surface modification, two stable domain states, with $\vec{P}$ in opposite directions and parallel to $\vec{E}$, were obtained. Since $\hat{n}$ is perpendicular to $\vec{P}$, it is then possible to switch the molecular orientation in the plane of the liquid crystal layer between two stable states by simply reversing the voltage across two parallel transparent electrodes (longitudinal biasing made). The large optical response due the high birefringence ($\Delta n \sim 0.2$) leads to a practical optical switching device (Figure 5; from Reference 48) similar in construction to that for ferroelectrics. However, the domain structures in liquid crystals are stabilized by surface mechanical forces, and not by bulk forces as in inorganic ferroelectrics, which is one of the reasons for their low voltage operation. Also compared to other liquid crystals such as cholesterics, the controlling voltages are even an order of magnitude lower due to the added linear $\vec{P}\cdot\vec{E}$ dipole term to the free energy equation.

Thus it is anticipated that ferroelectric liquid crystal optical switching materials will supplant the current ferroelectric PLZT materials in crossed-polarizer type devices. It is expected that other device configurations will be possible and that further improvements in switching speed can be achieved. The advantages of liquid crystals are lower cost, ease of fabrications, simpler operations, and lower power.

Other liquid crystals and switching device configurations have been shown to have large area transmissive mode optical switching potential. Although their potential for high speed do not seem as good as the ferroelectric liquid crystals, they are listed in Table 1 and will be discussed briefly since there could be other advantages that might make them practical optical shutters.

Twisted nematic liquid crystal devices can be produced by controlling the boundary properties of the confining ITO coated glass layers.(53,54) The device operates in a field effect mode and controls the optical rotation (90^o) by switching the local nematic director ($\hat{n}$) in a cooperative manner as shown in Figure 6. Although the fastest switching speeds reported so far are only ∿1 msec, they show reliable bistable behavior. As lower viscosity and thinner liquid crystal layers are developed these times are expected to improve somewhat. The twisted nematics are the liquid crystals used in commercial display devices.

A similar effect to the twisted nematics is found in cholesteric liquid crystals in that the nematic director twists. However, in the case of cholesterics this occurs due to the chirality of the liquid crystal and not by boundary anchoring conditions. By controlling the alignment of the molecules at the boundaries ($\hat{n}$ normally parallel to boundary), either homogeneous (parallel) or homeotropic (perpendicular) boundary conditions are established. When an electric field is applied to a cholesteric of positive dielectric anisotropy, several clear-to-scattering transitions can be obtained depending upon the boundary conditions and the type of texture (Grandjean and focal conic) obtained. Switching response times on the order of 10μsec have been obtained.(55) Although there are no commercial devices based upon this cholesteric-nematic transition (discovered and developed by

Xerox(56)), there could be some potential light switches used in a cascade fashion in an optical device where the numerical aperture were small enough. In such devices there is no need for polarizers.

The addition of dichroic dyes to liquid crystals have been used in two ways for effecting optical changes. In the first instance, a dichroic dye (elongated molecules) aligns itself with the similarly shaped liquid crystal molecules and thus switch with them. The dichroic dyes have an absorption anisotropy ($\Delta\alpha$) in the same manner as the dielectric anisotropy (ΔE or Δn). Dichroic liquid crystals (usually termed a guest-host system) can be tailored to have different absorption spectra and have been used in all three types of liquid crystals - nematics,(57,58) cholesterics,(59,60) and smectics.(61) Their speed of switching in a field effect mode is expected to be the same as the host liquid crystal. Because the dichroic ratios are not very high, contrast ratios of only about 10-100:1 are obtained. However polarizers are not needed in certain device configurations. The absorption of light by the dye in the maximum transmission state, however, can be appreciable and can produce color distortion.

A second way to use dichroic liquid crystals for light switches is to use the absorption capability of the dye to accelerate the heating of a liquid crystal so that it undergoes a rapid transition to an isotropic phase. Recent work(61) shows that smectic A-isotropic transitions can be switched in times as low as 5μsec and that the dye also adds to the overall optical density change. Although the contrast ratios are low (<100:1), much more work is needed to evaluate their potential.

A final method for optical switching based on liquid crystals involves scattering in inhomogenous media. Craighead et al.(62) have shown that by dispersing a nematic liquid crystal in a composite medium (see Figure 7) which has through-pores with sizes on the order of a micrometer, by field effect switching the liquid crystal can switch from a state where the refractive index is the same as the medium to one where $\Delta n \sim 0.2$. Such a change produces a clear-scattering transition. Although switching times of ∿1 msec were obtained, further improvements are conceivable.

The only other class of materials which alter the transmission state of the light and have potential for fast optical switching are the ferrimagnetic garnets. Based upon Faraday rotation of light in a magnetic field, a bistable optical switch is obtained by 90° rotation of light between appropriately placed polarizers (see Figure 8). Bi-doped iron garnet films have been developed by Litton Industries(15) for possible application in a variety of optical display and data storage and handling applications. The main advantage of the technique is its fast speed with 0.1 to 1 μsec switching times already measured. The drawbacks, though, are its high optical absorption (trade-off between film thickness and optical rotation), transverse quadrupole electrode structure, need for magnetic field, and the high cost of just the film since it must be grown on a single crystal substrate. Thus the outlook for practical magneto-optic effect devices is not as good as the previous materials.

Of the reamining possible materials/proceses to be considered from Table 1, no optical switching devices have yet been reported. Thus the discussion will be more speculative. The general areas to be considered are electrochromics, insulator-metal transitions, rapid metal deposition, and nonlinear optical effects in materials. It should be noted that each of these potential fast switching processes involves either absorption or reflection but not transmission. As nature would have it, the better solutions (and reflection is the best) present the bigger problems.

Considering electrochromics, it is initially seen that this covers a wide range of materials and processes. Electrochromism is defined as a reversible change in the optical absorption of a material resulting from an applied electric field or current. The physical mechanisms for electrochromic behavior vary for different materials. The types of materials include solids and liquids as well as organics and inorganics. An extensive review of electrochromic materials and phenomena has been given by Chang.(63)

In the broadest sense of the definition the dichroic dyes in liquid crystals (as discussed above) are electrochromics since an electric field can effect a change in absorption. Another variation on this idea, and one not yet tried, would be to put a dichroic dye in the liquid crystal/inhomogeneous medium scheme (as in Figure 7). In this situation there would be a combination of scattering and absorption. The scattering would increase the total path length of the light within the layer and thereby increase the total absorbance of the layer. It is not easy to predict the increase in contrast ratio that would be obtained but even a modest increase in a cascade-n-layer configuration is important since $O.D. \sim (C.R.)^n$.

Electrochromic processes based on charge transfer absorption should be extremely fast since they are based upon electronic processes and not the movement of atoms or molecules. To a lesser degree electrochromic processes dependent on short range diffution ($\sim$1-10Å) followed by electron transfer might be expected to have response times in the μsec range. Presently electrochromic processes based upon double-charge injection (eg. protons and electrons into WO_3(64-66)) are much too slow ($\sim$1-100msec response times) since diffusion must occur over thousands of angstroms. Thus new approaches, based upon charge storage within a material at an inactive site and release activated by a combination of laser beam and external forces (eg. electric fields or heat), should be investigated.

Although charge transfer absorption processes in both organic and inorganic materials have been studied for a long time,(63) the only reports which indicate the possibility of fast optical switching are semiconducting organometallic solid films based upon TCNQ (tetracyanoquinodimethane). Potember et al.(67) initially discovered that Cu-TCNQ films could be rapidly switched from a high resistance state (2MΩ) to a low resistance state (200Ω) at an electric field strength of 4000V/cm. This threshold bistable switching behavior occurred in $\sim$25nsec, has a non-volatile memory, and can be reversed by the application of a second current pulse with similar switching speeds. Based upon further studies(68-70) it has been shown that the rapid transformation results from the charge transfer process due to the field induced redox reaction,

$$\underset{\text{(high } \rho\text{, colored)}}{[Cu^+(TCNQ)^-]_n} \rightleftarrows \underset{\text{(low } \rho\text{, clear)}}{Cu^o_x + [Cu^+(TCNQ)^-]_{n-x}} + (TCNQ^o)_x$$

where $x \approx 0.3$. Furthermore, they demonstrated that similar behavior was found for Ag-TCNQ, that this latter material underwent a colored-clear transition under laser irradiation, and that reversible switching times of 5nsec were recorded. Although no data were given on the optical density change, it must be high since a good percentage of the material is apparently converted in the switching process. More work is clearly needed to determine the feasibility of this process for nsec time optical switching.

Electrochromic processes based on long-range charge injection have been studied for some time. For the case of WO_3 colored by proton and electron injection, the electrochromic double-injection process is given as,

$$\underset{\text{(clear)}}{WO_3} + xH^+ + xe^- \rightleftarrows \underset{\text{(blue)}}{H_xWO_3} \quad (x = 0 \text{ to } 1)$$

The materials that exhibit this behavior are generally transition metal oxides which are either reductively colored (W, Mo, V, Nb, Ti) or oxidatively colored (Ir, Rh, Ni, Co, Cr). The two most extensively studied are those based on "WO_3" and "IrO_2". The quotation marks are used since the material chemistry is usually ill-defined and yet very much related to the mechanism and dynamics of the optical switching. Some of the reasons for this difficulty stem from the fact that the electrochromic behavior is very highly dependent upon the preparation history of the sample and its subsequent interaction with the atmosphere during handling and surrounding layers in a device structure.

Current work on WO_3 thin films(71) show that the variability in coloration and bleaching properties are directly related to low density void network structures which are highly aligned perpendicular to the film surface. Such fast ion conduction paths can explain all of the observed electrochromic phenomena in tungsten oxide film devices. They also could provide the basis for fast optical switching.

It has been shown that significant amounts of hydrogen can be stored in as-deposited WO_{3-y} films(71-73) at inactive sites (H_x:WO_{3-y}). Transparent films (slightly yellowish in transmission) can be prepared with y = 0 to 0.3 while x can be as high as 0.2 to 0.5 depending upon preparation conditions.(72,73) The hydrogen contents are a combination of hydrogen included during deposition (eg. reactive sputtering in H_2 atmosphere) and post-deposition hydration;

however, the exact location within the thin film structure is unknown. Experiments on the coloration of these initially transparent films under UV-excitation(73-75) indicate that the coloration does occur by the transfer of hydrogen from an inactive to an active (bronze structure) site. Although the speed of the UV-coloration process was not measured it is expected to be very fast. If the movement of hydrogen were small (such as single jump or molecular rotation), the jump frequency would be in the microwave range ($\sim 10^{-9}$sec). No experiments have been reported on the laser or laser-assisted excitation.

The absorption spectra of WO_3 films have been measured by a number of workers with typical ones given in Figure 9. As seen the optical density is wavelength dependent but quite high throughout most of the visible spectrum and decreases as the blue region is approached. It is also noted that the crystalline films have a considerably higher O.D. especially at low energies due to the higher concentration of free electrons as compared to the amorphous films where electrons are nearly all localized. This increase is probably due to reflection resulting from an insulator-metal transition.

Although other materials may show similar behavior, the WO_3-based ones are the most extensively studied and already indicate the potential for fast optical switching. Obvious areas of future work include laser transformation studies as a function of electric field, temperature, and the preparation conditions of the samples. Since the higher the hydorgen content the greater the O.D. change, ways of increasing H-content in films, either during deposition or post-deposition processing (eg. mild ion-implantation in H_2-plasma discharge), by controlling the film structure should be tried.

For the amorphous "WO_3" films discussed so far, and on which most of this thin film literature exists, the layers act as true electrochromics in that a large absorption change occurs. However, for crystalline $H_x WO_{3-y}$ films where x > 0.5, the material acts as a free-electron metal.(76) [In both cases other metals such as Na, Li, K, Ag, Tl can be substituted for the hydrogen.] The reflection mode is preferable to an absorption mode for an optical switch, as discussed before, and thus the studies suggested above should be carried out for both amorphous and crystalline films. For the insulator-metal approach with crystalline films, a much thinner layer would be sufficient since the penetration depth of visible light into a free electron metal is very low. But in order to obtain the Drude metal state, a higher value of x is needed. This approach has the possibility of being a fast and practical optical switch.

Insulator-metal transitions have been the subject of theoretical and experimental investigations for a number of years.(77) Most of the materials that display this phenomenon do so at either high temperatures or high pressures. And in the case of the Morin transition the insulator-to-metal transition occurs as the temperature is decreased. Of the materials/mechanisms for insulator-metal transitions, the one that seems most practical for optical switching is the crystalline H_xWO_{3-y} as discussed above. Two additional mechanisms that should be considered are: (1) threshold electrical switching at SbSI junctions and (2) rapid crystallization of $BaPb_{1-x}Bi_xO_3$.

Threshold switching from a high resistance to a low resistance state has been found for a number of conductor/dielectric/condutor junction devices. In particular very fast switching times (<5nsec) were reported for SnO_2/SbSI/metal junctions.(13) Apparently as a result of a large space charge induced by the ferroelectric polarization, fast electron tunneling occurs. Whether or not this insulator-metal transition also results in optical reflection or an optical absorption transition is not known.

It is known that $BaPb_{1-x}Bi_xO_3$ when prepared as an amorphous thin film undergoes an insulator-metal transition as the film is crystallized to the perovskite phase.(78) The insulating amorphous phase has a modest absorption that increases at lower energies (rust color in transmission) while the crystallized films are metallic, and even superconducting at 13K. For sufficiently thin films (∿1000Å) the film is quite clear. If such a film were crystallized at rates of 1-10m/sec then transformation times of a μsec or less would be achieved for optical switching. Such rapid transformations have been observed in thin films and can be thermally driven both by the absorbed energy from the laser beam(18,79) as well as the released energy stored in the film.(80) This transformation is obviously not reversible.

Another method for obtaining a fast optical switch acting in a reflective mode is to employ laser-enhanced metal deposition. Recent developments in laser-enhanced electroplating and electroless plating of metal films have demonstrated that deposition rates on 10μm/sec can be achieved.(81) Thus the time to plate a 100Å film would be about 100μsec. Whether rates of deposition several orders of magnitude higher are possible will have to be seen. Also questions about laser energy absorption, energy thresholds, etc., would have to be considered.

The final area to be discussed is the more general area of nonlinear optical effects. Electro-optic effects such as the linear Pockels and quadratic Kerr effects are nonlinear but what is of concern here are enhanced effects even greater than those. Much of the optical properties of materials have been determined under relatively low light conditions. Much less is known about nonlinear optical effects under intense optical or optical plus dc fields. Although there have been reports of collective molecular reorderings, eg. in nematic liquid crystals(82,83) and ferroelectric polymers,(7) the experimental and theoretical results reported are still limited.(84,85) An example of a nonlinear optical effect prediction that remains to be proven (or disproven) is Platt's(86) hypothesis that a large electrochromic effect would occur in organic dyes containing long chains of conjugated bonds. In particular, he predicted that for strong electric fields of 10^6-10^7 V/cm their absorption spectra would shift thousands of angstroms. Although shifts of only ∿10Å have been found, it could well turn out that his prediction could come true in some new class of materials. The ability to predict new nonlinear optical properties is not good. However, this area must continue to be explored since it holds potential for major advances in fast optical switching.

V. CONCLUSIONS/RECOMMENDATIONS

An assessment of materials and materials based systems for fast acting optical switching has been made within the general framework of the ways that light can be altered - transmission, absorption, and reflection - and the driving force for the alteration. The possible specific materials/processes within this classification scheme are presented in Table 1. Of these, the four materials types which appear to have the best potential for improved fast acting optical switches are: (1) ferroelectric liquid crystals; (2) organometallic films containing charge transfer complexes, which undergo field-induced redox reaction; (3) inorganic electrochromic films which undergo insulator-semiconductor or insulator-metal transitions due to short range diffusion; and (4) inhomogeneous media in which the inhomogeneity is on the order of the wavelength of visible light.

For alterations in the transmission of light, rotation, retardation and scattering effects are usually large for materials which show a large dielectric anisotropy and shape anisotropy. In the types of switching devices considered in this report, it is necessary to move molecular units, domains, etc. Due to constraints of the surrounding matrix, the degree of interaction of the driving force (eg. electric field) with the optically active unit, size of the units, etc., the switching speeds are at best (presently) in the low μsec range. These times are found in liquid crystals where there is the best combination of dielectric and structural anisotropy, low viscosity, and degree of alignment under an external force. The best times in inorganic ferroelectrics seems to be about 10μsec and further improvements are not expected. Lower times are expected in liquid crystals due to possible: nonlinear effects under high optical excitations in combination with threshold electric fields; increases in dielectric anisotropy (eg. new ferroelectric liquid crystals); and decreases in their viscosity. The drawbacks to devices based on transmission effects are: absorption and damage threshold in polarizers (needed in materials systems based upon rotation and retardation); angle-of-incidence is critical; wavelength dependence of the various processes; and device construction appears complex and expensive (eg. PLZT goggles).

For optical switches based upon absorption effects, the most promising materials/mechanisms are those generally classified as electrochromics and are ones in which the electrochromic process is based almost totally on short-range diffusion and charge transfer processes. Electrochromics based upon a double charge injection mechanisms, for instance, are much too slow due to the slow ionic diffusion process over large (>1000Å) distances. Ultimately the speeds for such local charge transfer processes can be quite fast with values as low as 5nsec reported for CuTCNQ. In a somewhat similar fashion it is possible that inorganic electrochromics could show similar behavior in which the ionic specie leading to a charge transfer process is put into the structure during deposition and is switched from an inactive to an active site by a combination of external and internal electric fields. A third possibility has been suggested in which an inhomogeneous, porous media is filled with a material that has a dielectric anisotropy that can be rapidly switched and would have one state with a good refractive index match with the porous host. In any of these processes the effects of heating under the intense absorbed radiation would have to be considered. Also for the charge-transfer absorption processes the absorption coefficient varies considerably with wavelength. The porous media approach is more broad-band.

Although reflection changes are superior solutions, since heating effects are small and metallic reflection is broad-band, there are no materials properties yet reported with fast switching tims. Since primarily insulator-metal transitions have to be considered, the materials/mechanisms available are limited. The most promising ones are of the electronic type, eg. V_2O_5 and crystalline WO_3, the latter potentially possible in a manner similar to that above for electrochromic effects.

In a general sense the problem of eye protection against fast acting and intense optical radiation is a very difficult problem. Lasers are continually being developed with higher energies, shorter pulse widths, and can be at virtually any wavelength throughout the visible range. The solutions suggested above are far from perfect and require considerably more research. However, such μsec acting switches could still be important and, if cheap enough, be useful for other applications such as a replacement for PLZT flash-blindness goggles, welding goggles, and "medium-energy" lasers. Ultimately one needs a process which acts at the speed of light and none of the processes considered in this review have that potential since there is always a unit (atom, molecule, etc.) displacement which must take place.

Mainly reversible processes have been considered which is good from a practical device viewpoint. The reason for this is probably related to the fact that any fast switching process usually has a very low activation energy to overcome in order to switch. Thus reversibility is quite likely since the reverse process has, in turn, usually a low activation or perhaps all that is needed is to turn off the driving force and the internal forces (eg. anchoring energies for liquid crystals) will be sufficient to restore the material to its original state.

In addition to the solutions suggested in this report, there may be some other, new solutions which were not covered. The old concepts of selective filters or dyes are unacceptable when a number of wavelengths must be protected against. This is due to the poor selectivity ($\Delta\lambda$) of such materials, and thus their total absorption is too high. In laser holography and diffraction optics lies a double solution. First, since it is a diffraction effect the radiation is reflected. Second, the diffraction selectivity is very good ($\Delta\lambda$ small) and thus multiple wavelengths can be reflected without significant loss in transmission. This approach is currently being pursued by several contractors (eg. Hughes) and will not be described any further here. Apparently, though, this approach has its set of problems.

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Table 1

Classification of Potential Fast Optical Switching Materials/Processes

SECONDARY EFFECT	OPTICAL PROPERTY	T	A	R
Internal Electric Field	Optico-optic	•nonlinear optical effects (eg. cooperative domain or molecular realignment)	•nonlinear optical effects (eg. Platt's Prediction, photochromics, charge transfer in organometals)	
External Electric Field	Electro-optic	•optical rotation in LC •optical retardation in LC and FE •optical scattering in LC and FE •nonlinear electro-optic effects	•electrochromism - $H_x{:}WO_{3-y} \rightleftarrows H_xWO_{3-y}$ (amorphous) - organometallic films - dichroic dyes in LC	•Insulator-metal transition - $H_x{:}W_{3-y} \rightleftarrows H_xWO_{3-y}$ (crystalline) - SnO_2/SbSI/metal •Rapid Deposition
Heat	Thermo-optic	•ordered-isotropic transition in LC		•Insulator-metal transition - rapid crystallization
Magnetic Field	Magneto-optic	•optical rotation in ferrimagnetic garnets		

FE = ferroelectric, LC = liquid crystal

FIGURES

Figure 1	The calculated total intraocular energy as a function of range for two different lasers (Nd:YAG and ruby) and for three intrabeam viewing conditions [M-7 binoculars, 7mm pupil diameter (nightime unaided viewing), and 3mm pupil diameter (daytime unaided viewing)]. The range calculations were based on the lasers emitting 100mJ/pulse with a beam divergence of 0.25 mrad. The horizontal lines show the total intraocular energy required to produce the specified response as described in text (from Reference 2).
Figure 2	(a) General device configuration for light transmission and extinction as controlled by 90° optical rotation and half-wave retardation. (b) Specific device configuration for half-wave retardation in PLZT, leading to maximum ΔO.D., based upon changes in Δn due to partial switching along the polar axis (from Reference 29).
Figure 3	Configurations and polarization states for pratical ferroelectric optical switching devices (from Reference 3, p. 304).
Figure 4	Three general types of liquid crystals (from Reference 23).
Figure 5	Schematic of the sample geometry showing UP (extinguishing) and DOWN (transmitting) domains. A positive voltage moves the domain wall so the DOWN region grows (from Reference 48).
Figure 6	Twisted nematic field effect optical switching configuration (from Reference 3, p. 409).
Figure 7	Cross-sectional schematic of inhomogeneous medium with liquid crystal contained in pores and switched by transparent conductor electrodes (from Reference 62).
Figure 8	Operation of magneto-optic light switch based upon Faraday rotation (from Reference 15).
Figure 9	(a) Optical density vs. photon energy for amorphous and crystalline WO_3 films in both virgin and colored states (from Reference 75). (b) Electrical resistivity vs. metal concentration in the tungsten bronze structure (from Reference 76).

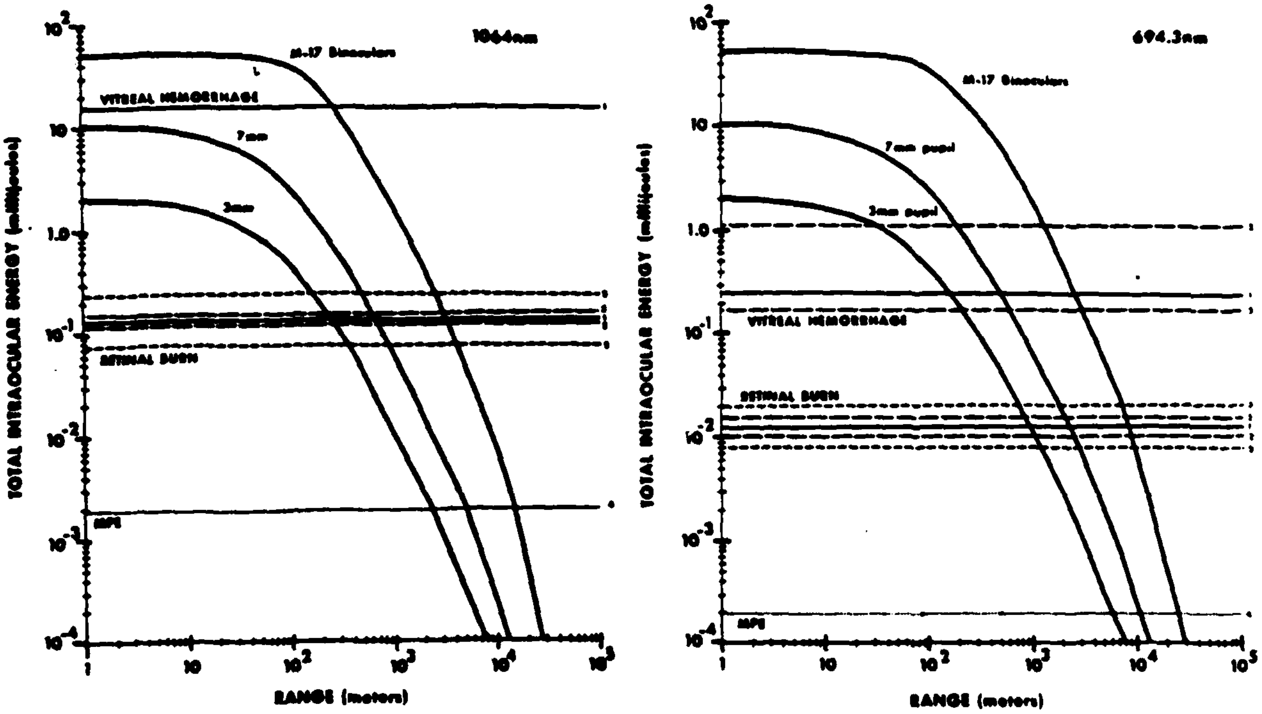

1064nm
M-17 Binoculars
VITREAL HEMORRHAGE
7mm
3mm
RETINAL BURN
MPE
TOTAL INTRAOCULAR ENERGY (millijoules)
RANGE (meters)
10^2
10
1.0
10^-1
10^-2
10^-3
10^-4
1
10
10^2
10^3
10^4
10^5
694.3nm
M-17 Binoculars
7mm pupil
3mm pupil
VITREAL HEMORRHAGE
RETINAL BURN
MPE
TOTAL INTRAOCULAR ENERGY (millijoules)
RANGE (meters)

Figure 1

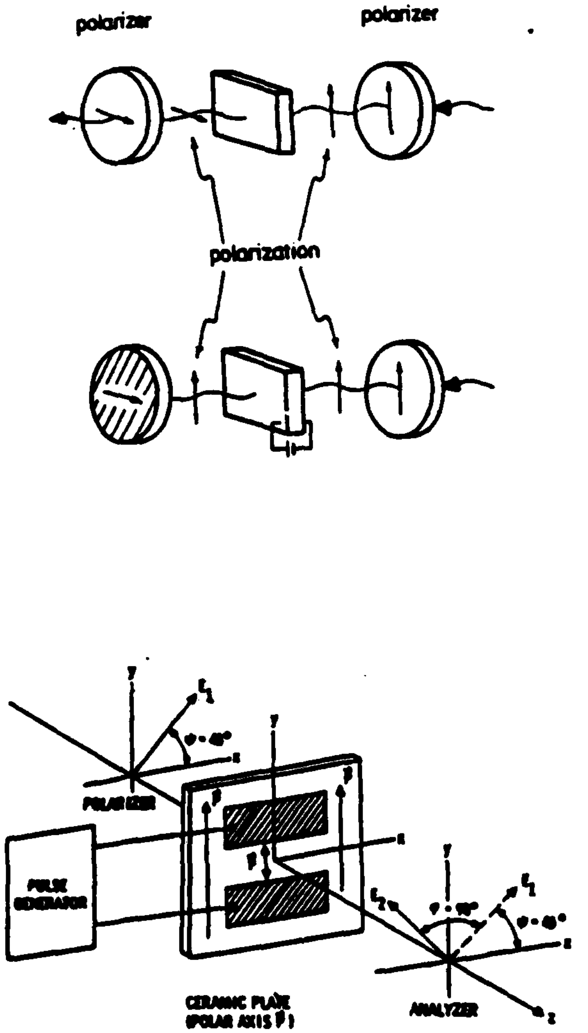

polarizer
polarizer
polarization
y
E_1
$\varphi = 45°$
x
POLARIZER
y
P
P
x
PULSE GENERATOR
P
y
E_2
$\varphi = 90°$
E_1
$\varphi = 45°$
x
CERAMIC PLATE (POLAR AXIS P)
ANALYZER
z

Figure 2

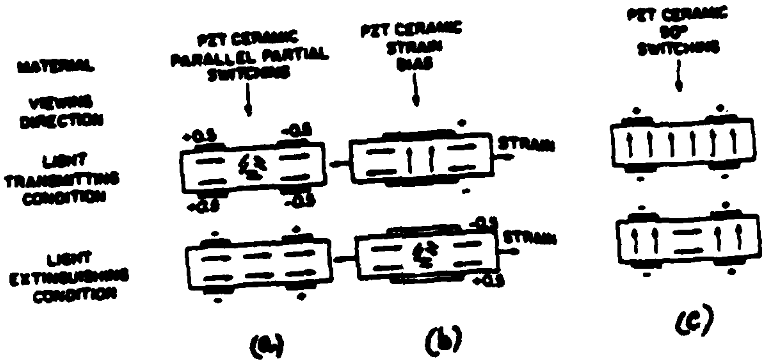
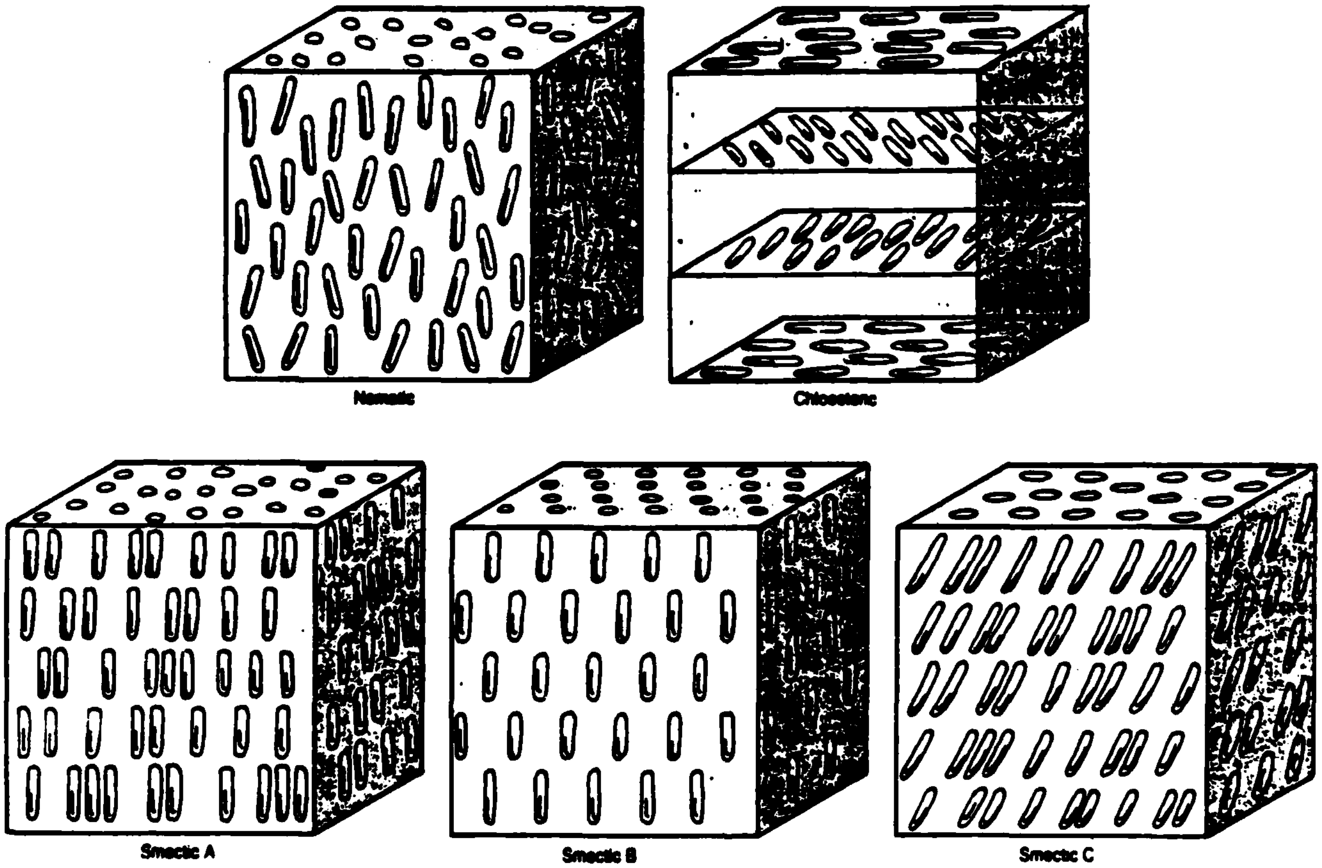

MATERIAL
VIEWING DIRECTION
LIGHT TRANSMITTING CONDITION
LIGHT EXTINGUISHING CONDITION
PZT CERAMIC PARALLEL PARTIAL SWITCHING
PZT CERAMIC STRAIN BIAS
PZT CERAMIC 90° SWITCHING
+0.5
-0.5
+0.5
-0.5
STRAIN
STRAIN
-0.5
+0.5
(a)
(b)
(c)

Figure 3



Nematic

Cholesteric

Smectic A

Smectic B

Smectic C

Figure 4

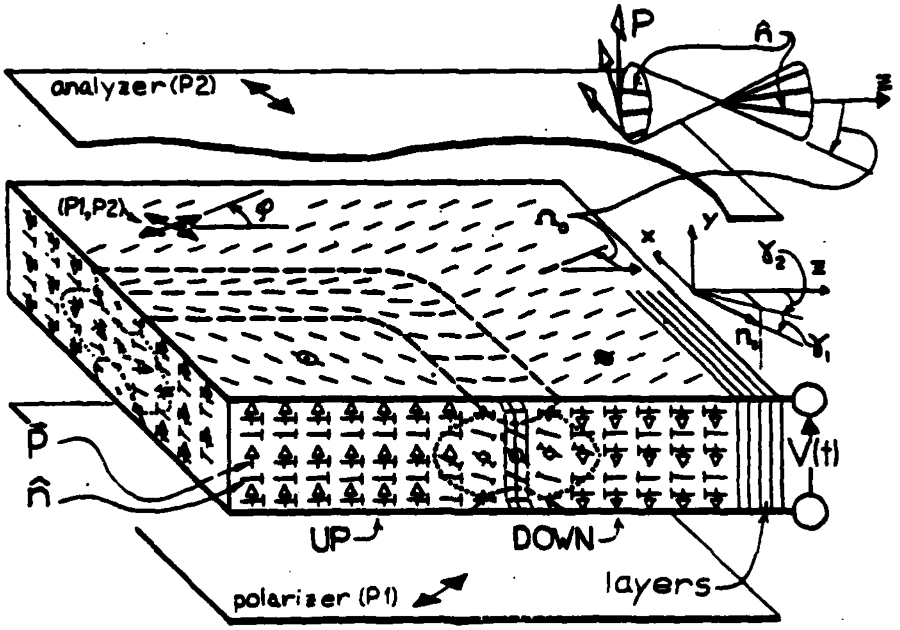

P
n̂
analyzer (P2)
z
(P1,P2)
φ
Ω
y
x
γ2
z
n
γ1
p̂
n̂
V(t)
UP
DOWN
polarizer (P1)
layers

Figure 5

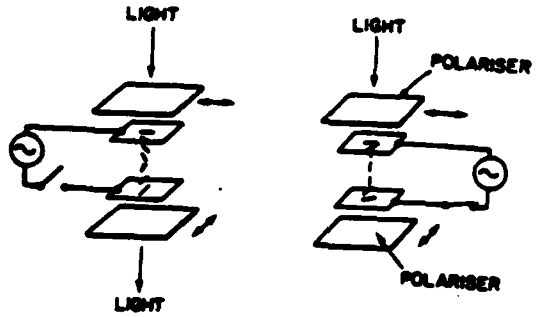


Figure 6

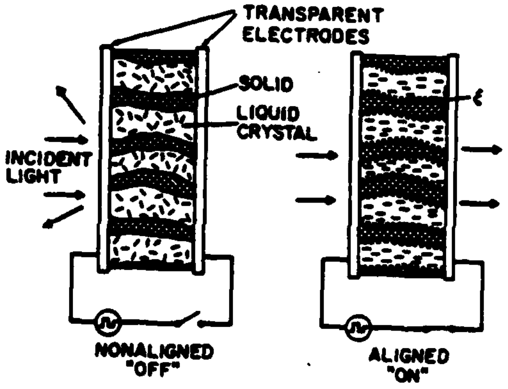

TRANSPARENT ELECTRODES
SOLID
LIQUID CRYSTAL
ε
INCIDENT LIGHT
NONALIGNED "OFF"
ALIGNED "ON"

Figure 7

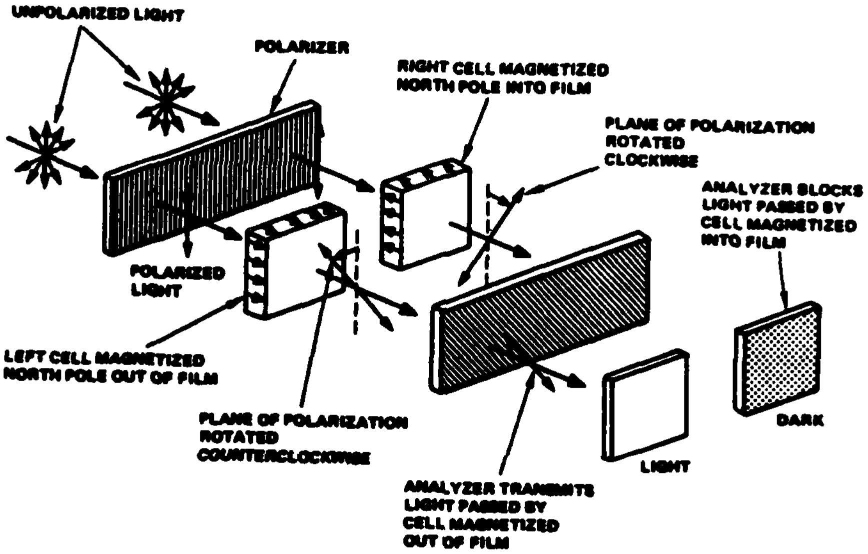

UNPOLARIZED LIGHT
POLARIZER
RIGHT CELL MAGNETIZED NORTH POLE INTO FILM
PLANE OF POLARIZATION ROTATED CLOCKWISE
ANALYZER BLOCKS LIGHT PASSED BY CELL MAGNETIZED INTO FILM
POLARIZED LIGHT
LEFT CELL MAGNETIZED NORTH POLE OUT OF FILM
PLANE OF POLARIZATION ROTATED COUNTERCLOCKWISE
DARK
LIGHT
ANALYZER TRANSMITS LIGHT PASSED BY CELL MAGNETIZED OUT OF FILM

Figure 8

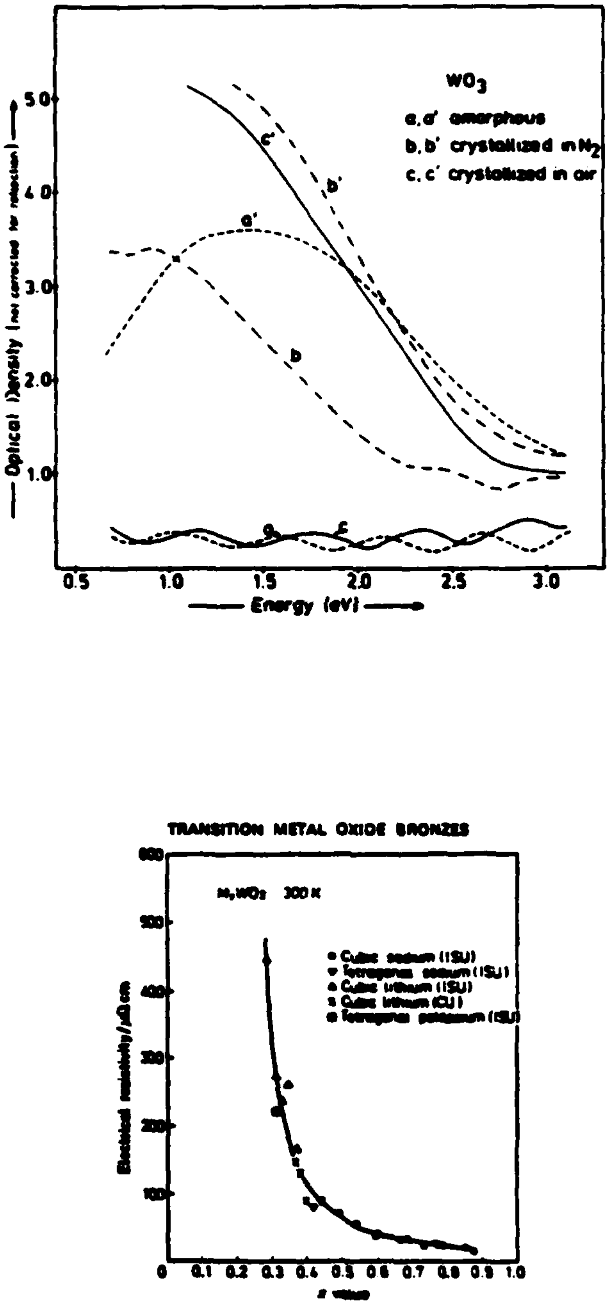

WO$_3$
a, a' amorphous
b, b' crystallized in N$_2$
c, c' crystallized in air
c'
b'
a'
b
a
c
Optical Density (not corrected for reflection)
5.0
4.0
3.0
2.0
1.0
0.5
1.0
1.5
2.0
2.5
3.0
Energy (eV)
TRANSITION METAL OXIDE BRONZES
M$_x$WO$_3$ 300 K
Cubic sodium (ISU)
Tetragonal sodium (ISU)
Cubic lithium (ISU)
Cubic lithium (CU)
Tetragonal potassium (ISU)
Electrical resistivity/μΩ cm
600
500
400
300
200
100
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
x values

Figure 9

MED

8