Research on Nonlinear Optical Materials: An Assessment

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Research on nonlinear optical materials: an assessment

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The seven papers making up this assessment are based on the Workshop on Nonlinear Optical Materials held in April 1986.

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I. Introduction

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A workshop on nonlinear optical materials was held in Annapolis, Maryland, 28–29 Apr. 1986. Five panels evaluated the following areas of nonlinear optical material research: (1) multiple quantum well structures, (2) bulk direct gap semiconductors, (3) photorefractive and liquid crystal materials, (4) inorganic materials for optical mixing processes, and (5) organic materials. In addition to these areas of discussion, fundamental limits on nonlinear optical materials and processes were considered by a sixth panel. The workshop was organized by M. Dagenais (GTE Laboratories) and P. L. Kelley (MIT Lincoln Laboratory) and was sponsored by the Optical Society of America and supported by the National Science Foundation (Light Wave Technology, p.d. T. K. Gustafson; Solid State and Microstructures Engineering, p.d. D. Silversmith; Quantum Electronics, Waves and Beams, p.d. L. S. Goldberg; Division of Cross Disciplinary Research, p.d. F. Betz) and the Air Force Office of Scientific Research (Optical Physics, p.d. H. R. Schlossberg).

The motivation for the workshop came not only from the realization of the importance played by nonlinear optical materials in many of the applications of modern optical technology but also from a feeling that a concerted effort on materials is required to maintain the United States at the forefront of science and technology in this area. Some of the current applications of nonlinear optical materials include: frequency conversion (harmonic and sum frequency generators, optical parametric oscillators, sources based on stimulated scattering), beam steering, removal of beam distortion, image amplification and transformation, optical processing and control of optical signals, optical limiting and threshold detection, all-optical interconnects, optical computing, optical memories, and optical fiber communication and devices (e.g., solitons).

The goals of the workshop were to:

(1) Assess present research on nonlinear optical materials.

(2) Determine the requirements on material properties for applications to communications, optical computing, high average power harmonic generation, etc.

(3) Identify the limitations imposed by current technology and by fundamental physical principles.

(4) Define particular areas in which nonlinear optical materials limitations are critically inhibiting applications.

(5) Assess the current state of nonlinear optical material and device fabrication and evaluation facilities.

The major conclusions and findings are as follows. Based on the high rate and quality of worldwide publication in this area, it is clear that nonlinear optical materials research is a rapidly evolving field of great potential. In the areas of optical communications, signal processing, and optical computing, both bulk and multiple quantum well (MQW) III–V semiconductor materials (binary, ternary, and quaternary compounds) will play a significant role. Large 2-D arrays of nonlinear etalons and 1-D and 2-D arrays of semiconductor lasers are being developed and new growth techniques and structures are being studied such as quantum wires and quantum dots. Even though the major emphasis of the research will be on III–V compound semiconductors, this should not preclude continued support of II–VI semiconductor materials for visible and infrared applications. Photorefractive materials will continue to play a key role in optical signal processing and real-time holography including phase conjugation. Some of the important scientific questions concern details of charge transport, achievable speed of response, and sensitivity. There appears to be an opportunity for improving response times using photorefractive effects in semiconductors involving the excitation of deep traps such as Cr in GaAs and Fe in InP. For slower speed applications, work on liquid crystal light valves is concerned with improving resolution and gaining a better understanding of the relation between molecular and macroscopic properties as well as of the trade-off between dynamic range and speed of response. To extend the spectral coverage of coherent sources, it is often more convenient to convert the available laser frequencies in a nonlinear crystal than to develop new laser systems; either inorganic or organic materials can be employed for this purpose. For near-term applications in the visible and the ultraviolet, beta barium borate, potassium niobate, potassium titanate phosphate, and L-arginine phosphate are the most promising crystals; for applications in the infrared, chalcopyrites, synthetic periodic materials, and Tl_3AsSe_3 appear to be the materials of choice. The field of organic and polymeric nonlinear optical materials is still in its infancy and much work remains to be done to fully understand their nonlinear response. Concerning the fundamental limits on nonlinear materials, it was concluded that each application requires its own specialized class of nonlinear materials and it was believed that not all the opportunities for new physical processes and novel structures have been exploited. This is reinforced by estimates for resonant nonlinearities which show that there is a large difference between known nonlinear coefficients and values obtained from theoretical optimization.

In general, the area of nonlinear optical material research is a multidisciplinary one; there is a strong need for interaction between physicists, chemists, optical and electrical engineers, and materials scientists. There also needs to be a synergism between materials

growth, experimental evaluation, and theoretical modeling. All the panels strongly recommended that funding for research be provided in such a manner that it enhances interactions between disciplines, and between academic and industrial research groups. For all the categories of materials that were considered, it was unanimously agreed that the unavailability or scarcity of appropriate nonlinear optical materials is severely restricting the progress and growth of the field. As a means of remedying this problem, it is suggested that government funded institutes, or centers of excellence within a university, be created to grow and characterize nonlinear optical materials in a systematic fashion. These materials should then be made available to the whole scientific community.

II. Bulk Semiconductors

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II.1. Introduction

The first experimental studies of optical bistability in semiconductor materials were reported for GaAs[1] and InSb[2] almost simultaneously in the late 1970s. Since then the possibility of using light to control light in these important materials has led to considerable activity, both theoretically and experimentally. Progress in the understanding of the nonlinear properties of GaAs and InSb has led to the construction and study of multiple quantum well structures (e.g., GaAs/GaAlAs) as well as the study of other nonlinear materials such as CdS, InAs, and HgCdTe.[3] The present state of the art in these materials for the realization of such devices as the optical transistor and digital optical memory element is about at the stage semiconductor electronics was twenty-five years ago; the latter, of course, has led to contemporary computer and communication technology.

In this section we first describe the range of applications for which the nonlinear optical properties of bulk semiconductors are of interest. Included here is a discussion of the distinction in applications between bulk (including conventional heterojunction) and quantum well devices. Then we briefly review the properties and status of materials and devices with emphasis on etalons, waveguides, amplifiers, and bulk structures. Finally we suggest future directions and cite national needs for this important field of research.

II.2. Motivation for Research

One of the primary reasons for considering bulk semiconductors for nonlinear optics is that they combine an attractive figure of merit with materials and fabrication technologies that have benefited from an enormous number of man years of effort. This provides substantial leverage in achieving rapid progress in forming structures for important device demonstrations. Semiconductors are useful for applications from 0.3- to 12-μm wavelengths using a variety of materials systems. In the 1-μm wavelength range, there is the exciting possibility of combining electronic and optoelectronic devices with nonlinear optical structures (e.g., in GaAs or InP). For signal processing and computing applications, GaAs especially and also InP nonlinear structures are attractive because they are compatible with diode laser sources. For longer wavelengths, narrow gap semiconductors (e.g., InAs, HgCdTe) offer nonlinearities greater than those in the 1-μm range and have potential applications ranging from four-wave mixing to high power optical limiters.

Many of the applications for semiconductor nonlinear optics are in the optical communications and signal processing (computing) area. Here devices could be used for serial or parallel processing. Waveguide structures are particularly attractive for high-speed pipeline applications and for use in fiber systems. Examples include fast logic gates, optical switches and modulators (both as arrays and integrated with diode lasers), and laser amplifiers. In the area of parallel processing, 2-D arrays of etalon devices[4] and laser amplifiers[5] offer much potential. Applications include switch arrays, image processing, matrix multiplication, and signal correlation. For optical beam manipulation, bulk semiconductor devices are attractive. Here applications include phase conjugation, tunable filters, mode-locking elements, nonlinear interferometers, power limiters, and optical fuses.

Semiconductors are also ideal candidates to study the physics of nonlinearities. Examples include self-focusing, self-bleaching, and bistability effects. Furthermore, a new class of materials, semiconductor-doped glasses, has much potential and can be understood from a semiconductor physics point of view.

For a number of applications, it is relevant to draw

distinctions between bulk semiconductor and multiple quantum well (MQW) structures. Here, we use the word bulk to refer to single crystals as well as conventional heterojunction structures in which the energy levels are not quantized. Some advantages of the bulk materials include the greater maturity of the technology and availability of crystals/wafer. This implies that device concepts/materials can be tested more easily for much less expense and over a broad optical spectrum (e.g., MQW material is really only available for GaAs/GaAlAs; there is very limited availability of GaInAs/GaAs and CdTe/HgCdTe). Most importantly, for a number of applications, the enhanced nonlinear effects in MQWs due to excitons are difficult to exploit due to the high background absorption. If one must work at wavelengths considerably away from the exciton peaks, where nonlinearities are much weaker, it is not clear whether there is any substantial advantage to be gained from multiple quantum well vs conventional heterojunction structures. Thus it would be appropriate to demonstrate the same nonlinear devices (e.g., etalon arrays) using both materials approaches. The ease of fabrication and material availability of conventional structures may even outweigh any slight theoretical performance advantage of MQWs.

III.3. Review of the Field

There has been significant progress in the past few years in research on nonlinear optical mechanisms and devices based on direct band gap semiconductors, although considerably more effort is required before optimization of materials and devices is completed. Various types of nonlinearity such as free excitons, bound excitons, biexcitons, band filling and renormalization effects, two-photon band-to-band absorption, and thermal effects have been employed in a number of semiconductors to demonstrate optical signal processing.[3] These devices may use cavityless optical bistability, nonlinear etalons, or nonlinear waveguides. Other configurations are four-wave mixing, yielding phase conjugation, nonlinear interferometers (ring, Michelson, Mach-Zehnder), and nonlinear gratings. The laser amplifier may be employed as well as self-focusing, self-pulsing, self-bleaching, and induced absorption systems.

Free exciton saturation in GaAs,[6] bound exciton saturation in CdS,[7] biexciton two-photon absorption in CuCl,[8] the band filling nonlinearity in InAs,[9] InSb,[10] CdHgTe,[11] and thermal nonlinearities in CdS,[12] ZnS,[13] and ZnSe[13,14] have been extensively studied. Optical bistability and switching in all of these materials have been reported. Two-dimensional etalon arrays of switching elements have been constructed in GaAs (a 100×100 array with each element having a size of 9×9 μm).[4]

Glasses doped with microcrystallites of semiconductors are new materials for nonlinear optics.[15] The small crystallite size (tens to thousands of angstroms) leads to a very rapid carrier decay time and promise of devices with picosecond switching speeds. They are also very interesting for studying the physics of quantum confinement in all three dimensions. This can be realized by growing glasses containing semiconductor crystallites with uniform size distributions, thereby approaching the quantum dot limit. The nonlinear index of refraction as a function of frequency and its absorption coefficient have been measured in commercial color glasses and the nonlinearity is attributed to band filling effects.

A new type of optical bistable device with optical feedback, that uses an electrical input only to create population inversion and gain, has recently been demonstrated. An InGaAsP/InP laser amplifier has been operated as a nonlinear optoelectronic switch with 20-dB gain.[16]

Some of these devices work at room temperature (such as GaAs, ZnS, ZnSe, the doped glasses, and the diode laser amplifiers) and some at lower temperatures (CdS at 2 K, InAs and InSb at 77 K, CuCl at 15 K). The operating wavelength varies from 0.3 to 10 μm. The values of the index n_2, absorption coefficient α, and switching time τ vary considerably for these materials. However, a figure of merit, defined as $n_2/\alpha\tau$, does not vary much for all materials.

To date, the nonlinear semiconductor waveguide emphasis has been on measuring the optical nonlinearities. Existing experiments in essentially cw regimes on pure semiconductor GaAs, InP, and GaAs/AlGaAs waveguides have shown large thermal effects, in addition to the nonlinear electronic component, and further experiments with picosecond sources are needed to assess such waveguides for multigigabit information processing. Composite semiconductor materials, specifically semiconductor-doped glasses, also reveal a large thermal as well as electronic component when used in waveguide form. These composite materials are of special interest because the relaxation time for the electronic nonlinearity was found to be <15 ps, and because high quality waveguides are simple to fabricate. Two-photon absorption effects in low-loss waveguides (for example, ZnO) also look promising because the waveguides are low loss at low powers and have usefully large nonlinearities for waveguide devices.

II.4. Conclusions

The outstanding applications-related challenges to be solved are to reduce switching energy, increase speed, and achieve optimum match between laser sources and the resonant nonlinearity of interest. The outstanding physics challenges are to understand the interplay between electronic and thermal nonlinearities and to define clearly the difference between bulk and MQWs.

The future of nonlinearities for optical switching is defined by the fact that the ratio $n_2/\alpha\tau$ is more or less constant, with a value of 1000 cm^3/J (within a factor of 100) for most of the nonlinear processes. This suggests that a compromise should be made between power and speed; faster speeds require high powers and vice versa. When α has to be small, e.g., for waveguide applications, the operating wavelength is farther away

from resonance, resulting in smaller n_2. For etalon operations, larger n_2 is needed due to short material thickness, forcing operation closer to the material band gap and causing a larger α. The rule of thumb for operation of an array of pixels which will allow adequate dissipation of heat is $\simeq 100$ W/cm^2 on a cw basis. Of course, laser sources that match semiconductor nonlinearities are required for all these operations.

Research to optimize the nonlinearities will thus focus on quite different material properties in the different cases. It will also have a different emphasis depending on the ultimate goals. For example, optical signal processing will most probably employ 1-μm or shorter wavelengths; whereas infrared imaging systems will require limiters, tunable filters, etc. in the 3–10-μm range.

With regard to excitonic nonlinearities, future research should seek semiconductors having sharper room temperature resonances and faster carrier recombination times. We need a better understanding of the nonlinearities and their saturation characteristics to reduce the switching energy. Materials with larger excitonic energies could provide room temperature resonances. Surfaces or traps could enhance recombination; the exciton energy might also be made time dependent via bound magnetic polaron effects in diluted magnetic semiconductors such as CdMnS. The major emphasis of this research should be on III–V compound semiconductors. This should not exclude continued strong support of II–VI materials for visible and far-infrared applications.

To date, band filling has been carefully studied in InSb (5 μm), InAs (3 μm), and HgCdTe (10 μm). For applications, materials with gaps matched to other important laser transitions will be needed. Perfect thin layers with sharp band edges will be required. Research should also focus on techniques for controlling carrier lifetimes.

Free carrier nonlinearities are inherently fast (picosecond response) but weak,[17] although there have been predictions of considerably larger nonlinear coefficients in modulated structures in resonant conditions. Research should test various proposals for enhancing free carrier nonlinearities via modulation. There have also been suggestions that electronic phase transitions (the metal–insulator transition) or instabilities could enhance nonlinear behavior. These possibilities should be explored. Although weak, free carrier nonlinearities are fast and, potentially, can be controlled electronically.

Etalon based devices would benefit from studies of speed limitations, crosstalk limits, and dynamics of materials and devices. Technology developments are required in the growth of uniform layers, the fabrication of uniform arrays, heat sinking, and techniques for addressing pixels. The expectations are a 1000×1000 array in 1 cm^2 with 1 pJ per operation at 100 MHz for 10^{14} bits/s.

Passive waveguide geometries are much behind the etalons in technology development and in physical understanding. We need to characterize nonlinear waveguides, optimize the materials and geometry for particular requirements, and demonstrate prototypes.[18] Research in bistable laser amplifiers should focus on optimum designs and switching energy and speed and on the effects of spontaneous emission. One-dimensional and 2-D arrays with improved uniformity and frequency control are needed. The expectations are nonlinear devices for fast dynamic interconnects and recirculating optical processors.

Theoretical analysis is needed to complement experiments. Analysis of glitch rates, transverse effects, many-body approaches to band gap renormalization, intrinsic bistability, and bistability in four-wave mixing are all important research areas. Finally, investigation of optical nonlinearities at phase transitions and regions of electronic instabilities may lead to higher figures of merit than previously predicted.

Further understanding of basic materials and device physics will contribute immeasurably to developing new and useful nonlinearities.

The research will emphasize room temperature properties since nonlinear optic systems will usually operate there. However, we urge some funding for low temperature work as well since such experiments can be especially powerful in elucidating most mechanisms or phenomena.

II.5. National Resources and Needs

National resources for performing optical research on semiconductors are severely limited. Many universities testify to the shortage of qualified scientists and engineers in these fields. There is also a problem with regard to samples. Semiconductor material and microstructure growth are demanding, expensive endeavors. It is urgent that the United States remain competitive in this area since optoelectronic systems will clearly require new and improved materials. The training of scientists and engineers with strong backgrounds in semiconductor and optical science should be an important goal of the research programs sponsored by governmental agencies. There are also large needs for captial equipment to study such problems.

The research problems outlined above are highly interdisciplinary. For example, recent achievements in optical communications have been made by collaborating teams of physicists, chemists, electrical engineers, and materials scientists. Even greater interaction will be required to develop the optical data processing systems that are envisioned. Thus, the panel strongly recommends that funding for research on semiconductor nonlinear optics be provided in such a manner that it enhances interactions between disciplines and between academic and industrial research groups. In particular, research consortia with a formal structure for meetings, exchange of samples, characterization facilities, and industrial contacts (or participation) would appear to be an effective mode for encouraging collaborations. The Defense Advanced Research Projects Agency sponsored HgCdTe program is a model for such support which, through a series of regular meetings, briefings, sample exchanges,

and complementary research projects has developed a national program in focal plane array materials research. We envision a similar coordinated funding pattern for the semiconductor nonlinear optics work.

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III. Multiple-quantum wells

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III.1. Introduction

Recent advances in semiconductor growth techniques have made it possible to grow semiconductor heterostructures with atomic-scale control of the composition and thickness.[1,2] Quantum-well structures (QWSs) consist of ultrathin layers of semiconductors having different composition and grown alternately one after another. Because of this structure, the position of the electronic energy levels is modulated in the direction normal to the layers. If the modulation is deep enough the carriers are confined in the lowest band-gap medium. Quantum-size effects are then observed if the thickness of the latter layer is smaller than the characteristic length governing the quantum mechanics of the carrier such as the Bohr radius or the de Broglie wavelength (i.e., 10–100 Å in usual semiconductors).[3] The quantum-size effects significantly modify the electronic and optical properties of QWSs compared with those of the parent bulk compound. Enhanced responses to optical and electrical excitation have been demonstrated in QWSs.[4] More efficient emission characteristics resulting from the reduced dimensionality have been utilized in low-threshold or high-power QWS lasers.[5] The nonlinear optical properties of QWSs, which are reviewed in Sec. III.3 of this paper, are very promising for applications to optical signal generation, processing, and transmission.

III.2. Motivation for Research

A. Fundamental

The reduced dimensionality changes the physical properties such as the band structure, exciton levels, etc. leading to different linear, nonlinear,[6–8] and electrooptic effects.[9,10] These changes have important implications for electronics as well as optics. In particular, the quantum-well laser characteristics are quite different.

B. Applied

(1) Engineering of materials. Current examples include quantum confined Stark effect using a room-temperature exciton feature for modulation and bistability; room-temperature exciton for mode locking a diode laser[11]; band-gap shift to tune the wavelength of a multiple quantum well structure (MQWS) etalon to that of a diode laser. The ability to design properties may be the key to optoelectronic integration.

(2) Parallel processing using arrays of nonlinear-etalon gates or bistable elements.[12,13]

(3) High-speed (>5-GHz) serial processing for encryption and multiplexing and decoding at the receiver end. Bistable lasers that give high gain and keep the information in the optical domain are potentially useful.

(4) GaAs QWS lasers. There is a push to produce low-threshold index-guided lasers for both high-power laser arrays and optoelectronic integration. Presently high-power quantum-well structure (QWS) laser arrays have achieved 5-W cw room-temperature operation and 11-W quasi-cw (150-μs) operation. These gain-guided devices are good for pumping nonlinear optical materials. For improved mode properties and phase matching, index-guided lasers are needed. Some progress has been made using elegant processing procedures incorporating the flexibility of QWSs but more work is needed. For optoelectronic integration many lasers should be integrated on a chip. One of the major problems is to reduce the power requirements for each device. Buried GaAs/AlGaAs QWS lasers with 1.5–3-mA thresholds have been demonstrated and submilliampere thresholds are expected. GaAs/AlGaAs QWS lasers have already demonstrated higher reliability, higher efficiency, and a 3.4 times increase in wavelength tunability over conventional bulk double heterostructure lasers.

(5) Other. The other potential uses of nonlinear optics, such as phase conjugation applications, laser hardening, etc., may be facilitated or made possible by QWSs.

III.3. Review of the Field

A. Current Status

In the last few years linear optical properties, nonlinear optical effects, and electroabsorption of GaAs/AlGaAs QWSs have been extensively investigated experimentally and theoretically. Studies of similar effects in QWSs based on other material systems are just being started and preliminary results are very promising.

The special properties of QWS result from the effect of reduced dimensionality[14] on the absorption spectrum. The spectral density of states of single-particle bands has a steplike profile. This sharp edge can be used to increase the number of states participating in emission with direct implication on the characteristics (threshold and power output) of semiconductor lasers with quantum wells in the active region. The electron–hole correlation produces quasi-2-D exciton resonances with increased binding energy which are observed at room temperature contrary to what is seen in bulk compounds.[6] These resonances are very sensitive to external perturbations (optical excitation and electrostatic fields); unusually large changes of refractive index and absorption coefficient result.

Under optical excitation the exciton peaks are seen to saturate at low intensities ($I_s \leq 1$ kW/cm^2). The nonlinear optical processes exhibit femtosecond transients at room temperature because of the exciton ionization by thermal phonons and the change of relative magnitude of the basic physical mechanisms causing the bleaching of the resonance in two dimensions. At low temperature this also produces a blue shift of the exciton peak that only occurs in QWSs. Saturation of the absorption of QWSs has already been utilized in optical bistable etalons and in passive mode locking of semiconductor lasers.

As already mentioned, application of an electrostatic field either parallel or perpendicular to the direction of the layers produces large changes in the absorption spectrum.

For a field parallel to the GaAs/AlGaAs MQW layers one sees broadening and reduction of peak absorption due to field ionization, similar to that observed in bulk GaAs.[9] However in QWSs this is seen at room temperature, and a response time as fast as 330 fs has been demonstrated—approaching the fundamental limits of optical modulation by semiconductors. These effects have potential for very high-speed high-contrast sampling.[15]

For a field perpendicular to the layers a new effect is observed that is specific to QWSs: the quantum confined Stark effect (QCSE).[9] In this geometry the field induces a very large red shift (10 times the bulk Rydberg constant of bulk GaAs has been demonstrated). The QCSE has already been used for high-speed large-depth modulation of light (100 ps/10 dB has been demonstrated in QWS waveguides).[16,17] It has also been used to modulate the emission of a light emitting diode by action of the overlap of the carrier envelope-wave functions. A QWS in PIN structure can simultaneously operate as modulator and photodetector. This gives a means to measure the absorption by the photocurrent which in turn can be directly fed back to change the field across the QWS. This dual operation has been used in a new class of devices, the self-electrooptic effect devices (SEED), that have been used for low switching energy optical gates (and small arrays of gates), optical level shifter, wavelength-sensitive detector, and self-linearized modulators. Most of these devices have also been implemented in waveguide geometries, and demonstration of integration of several functions has been achieved (for example, integrated QWS laser-modulator structures).[18,19]

Other QWSs include nipis and strained, large-discontinuity (GaN, InN, ...), semimagnetic (CdTe, ...), and quasi-periodic semiconductors. The nipis are QWSs formed by periodic n- and p-doping in single-material or heterostructures (heteronipi). Due to the built-in field, they exhibit electroabsorption linearity in the applied field. A large change of optical constant can be induced at extremely low light intensity because of the long lifetimes. This has potential application of optical memories with intermediate holding times. The nipis are also widely wavelength tunable and the recovery times electrically adjustable.[20]

Very thin layers, lattice mismatched with respect to the substrate, can be grown with a high degree of perfection if the layer thickness is kept less than the critical strain necessary to form misfit dislocations.

An example of new properties introduced by strained superlattices is the work on $Si_{1-x}Ge_x/Si$ superlattices which extend the performance of Si-like avalanche photodetectors to $\lambda = 1.3$ μm. Their performance depends fundamentally on the lattice strain-induced reduction of the $Si_{1-x}Ge_x$ band gap.[21] Strain effects are being actively investigated in III–V strained-layer superlattices.[22]

Semimagnetic semiconductor QWSs of (Zn,Mn)Se and (Cd,Mn)Te have been grown by molecular beam epitaxy. The band-gap modulation in these systems is provided by varying the Mn mole fraction; as the Mn fraction increases, the band gap of the material increases.[23] The resultant alloy compounds cover a wide wavelength range while maintaining a direct band gap. Recently, excitonic saturation was demonstrated for QWSs in the (Zn,Mn)Se material system.[24] The binding energy and oscillator strength of excitons in this system are larger than for III–V materials such as (Al,Ga)As. Thus, although the excitonic resonance is more difficult to saturate, it provides a larger contribution to the index of refraction. The wide gap QWSs in the (Zn,Mn)Se system, which have an energy gap corresponding to $\lambda = 440$ nm, can support a maximum diffraction-limited device packing density of 4 times that of the (Al,Ga)As system.

In addition to the conventional nonlinear optical phenomena which have been studied in both III–V and II–VI QWSs, semimagnetic semiconductors provide a unique opportunity to exploit nonlinear limits of large magnetooptic effects resulting from the exchange interaction between the moments of the Mn ions and the conduction/valence band states. It is expected that the magnetooptic constants can be saturated in a manner similar to the optical constants. Novel devices based on the magnetooptic properties can be envisioned.

Quasi-periodic or incommensurate superlattices have just been realized in GaAs/AlGaAs and show interesting phonon lines principally using Raman scattering. It is important to investigate their electrical and optical properties and their potential for high-speed devices.[25]

B. Adequacy of Fundamental Knowledge, Materials Growth, and Characterization

Strong interaction between all three areas is essential.

1. Adequacy of Fundamental Knowledge

Much remains to be learned about QWSs, and much of it will be important for electronics as well as optics. Confinement in one, two, and three dimensions leads to many new interesting effects and changes in familiar effects: coupling between wells, tunneling, resonant tunneling, Stark shifts, transport properties, femtosecond dynamics, large (100-Å) Bohr-radius excitons, electroabsorption, electrorefraction, optical transitions, structure, etc. In the area of material aspects much remains to be done to study and improve layer roughness and interface quality. Techniques such as growth interruption at heterointerfaces and artificial perturbation of the growth kinetics need to be studied in more detail.

2. Adequacy of Materials Growth

In addition to continued growth studies using GaAs/AlGaAs, QWSs should be grown and studied by all conceivable techniques. Molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) are expected to continue to dominate and should be continually compared in terms of purity, uniformity, size, cost, ease, etc. Can atomic layer evaporation be used to grow large-area MQWs?

3. Adequacy of Characterization

It would help to be able to monitor surface roughness and clustering over larger areas, to separate whether features come from composition or strain, to measure composition within a few wells or a single well, to monitor fluxes of gases in MOCVD (by IR spectroscopy?), to use interband and/or capacitance spectroscopy, etc.

C. Device Limitations

By and large, QWSs exhibit equal or superior characteristics to bulk structures. The growth flexibility adds tailoring opportunities that often can be used to advantage.

1. Speed

The SEED has achieved 30 ns and may go down to 3 or even 1 ns. All-optical devices cannot use surface recombination involving diffusion perpendicular to the layers, but recombination centers may be introduced at the interface. Proton damage has worked well for mode locking diode lasers but not for bistable etalons. QWS lasers seem to modulate more slowly than bulk, contrary to theory. Note that slow low-power devices are better than fast high-power devices for some applications.

2. Damage Threshold

Damage is no worse in QWSs than bulk. Added flexibility sometimes can be used to reduce damage, e.g., use of Ga and Al interdiffusion to reduce heating of laser windows.

3. Size of the Nonlinearity

Bigger at 300 K than bulk.

4. Ease of Fabrication

Admittedly one pays the price of more expensive and difficult growth for all the other advantages.

5. Physical Properties

These are more pronounced and more flexible.

6. Background Absorption

This is as important to know below the band gap as the nonlinearity. It is usually phonon-assisted at room temperature: high-purity growth is essential.

7. *Thermal*

QWS lasers are less temperature sensitive. Heat sinking characteristics are little different.

8. *Wavelength Range*

QWSs are much more flexible with wider tuning ranges and new wavelength regions.

D. Significant Gaps in Effort or Knowledge

Much remains to be learned, e.g., band structure changes needed for calculating changes in properties, transport parallel and perpendicular to layers, many-body effects in quasi-2-D, Stark effect, linear electrooptic effect. Much remains to be tried, e.g., photochemical deposition to build in micron-resolution spatial features during growth; gas-source MBE; plasma-assisted MOCVD; multichamber MOCVD; new growth techniques, such as chloride chemical vapor deposition; new metal-organic sources, such as arsenic replacement.

One of the most exciting aspects of using QWSs is the ability to use novel processing techniques such as impurity-induced disordering, defect-induced disordering, *in situ* localized laser-controlled deposition and etching, and laser-induced (photothermal) disordering. These techniques, when applied properly, can produce integrated optoelectronic device structures, i.e., lasers, waveguides, modulators, detectors, couplers, filters, drivers, etc., all on a chip.

E. How and Where Should New Materials Be Grown?

Strong interactiveness between crystal growers and device researchers is essential. Service centers generally do not work. It is better to distribute five machines than to place them in a single service center.

Having more than one machine at one location is conducive to trying new ideas and materials. The first machine is usually dedicated and opened as seldom as possible.

The development of versatile *in situ* feature-definition capabilities is very important.

The purchase, safety protection, and operation (personnel, substrates, liquid nitrogen, etc.) of growth machines are expensive; additional support is needed to keep the United States lead, to educate students, etc.

III.4. Conclusions

A. QWS Physics is Fundamental and Exciting

The nature and magnitude of the physical mechanisms governing the optical and electronic properties of semiconductor nanostructures depend very critically on the dimensionality of these structures. Novel properties are expected to appear as the size of the structures is reduced and the energy levels are locally modified. In particular, nonlinear optical phenomena (such as stimulated emission, bleaching of excitonic absorption, electromodulation, and optomodulation) are increased in strength in MQWs due to the quantum-size effect and/or the reduction of dimensionality to two-dimensions [and in future possibly to one-dimension (quantum wires) and zero-dimension (quantum dot)]. Novel phenomena that do not occur in bulk materials (quantum-well oversaturation in heteronipis, e.g.) are expected.

B. QWS Effects are Important in Demonstrated Devices

Apart from the well-established superiority of QWS lasers, other important device applications have been demonstrated in bistable devices made from MQWs.

Whereas the first refractive bistable etalons differ by their tailoring flexibility from their bulk counterparts, the SEED is based on a unique novel property of MQWs, the decrease of transmission due to increased absorption.

C. Near Certainty of New Important Devices Using QWS

As well as the device technology that has already been demonstrated, MQW materials offer important potential for novel high-performance devices. Present research is pointing the way to future devices such as large arrays and integrated optical and optoelectronic devices incorporating several functions on a single chip.

D. Optical QWS Studies Provide Useful Data for Optical Electronics

Because similar quantum well structures are used for optical and electronic devices such as double QWS and superlattice-high electron mobility transport (SL-HEMT) devices, research on MQW optical structures will simultaneously advance the knowledge of high-speed electronic devices. This should be true not only for the GaAs/AlGaAs QWS but for other III–V systems. The close relationship between optical and electronic devices will prove to be important for optoelectronic integration.

E. Interactions Between Materials Growth and Device Development are Essential

The detailed nature of interfaces and the physical properties of the well material in MQW structures are inextricably related to device properties. The past success of this field can be attributed to strong interactions between materials and device scientists. We therefore strongly recommend that interactive material–device studies be continued and encouraged. This will stimulate the development of both novel device structures and material growth techniques.

F. Increased Funding Recommended

Because of the points listed above, this committee believes that the funding for research on MQW and other structures exhibiting quantum-size effects should be expanded. There are heavy costs associated with the purchase, installation (including safety features), and operation of the growth facility. It should be noted that there are major efforts in this area under way both in Europe and in Japan. At present, the United States has a strong position in this field, but this will not be maintained unless substantial resources can be allocated to this key area for future science and technology.

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IV. Photorefractive and liquid crystal materials

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IV.1. Introduction

This panel considered two separate subject areas: photorefractive materials used for nonlinear optics and liquid crystal materials used in light valves. Two related subjects were not considered due to lack of expertise on the panel: photorefractive materials used in light valves and liquid crystal materials used in nonlinear optics. Although the inclusion of a discussion of light valves by a panel on nonlinear optical materials at first seems odd, it is logical because light valves and photorefractive materials perform common functions.

Strictly speaking, one might define a photorefractive material as a material in which light induces a refractive-index change. Over the past fifteen years, however, the term has come to be understood to refer to a much smaller subset of such materials. We consider photorefractive materials to be those in which absorbed photons cause charge migration (drift, diffusion, hopping, etc.), the distortion of charge results in a space charge field, and the field modulates the refractive index through the electrooptic effect. All photorefractive materials must absorb light and have both mobile charges and a nonzero electrooptic coefficient.

Liquid crystal light valves consist of a layer of liquid crystal material, an electric field applied to the layer, and a means to obtain spatial modulation of the field. In optically addressed light valves the spatial modulation is obtained by shining light on a photoconductive layer in series with the liquid crystal medium. In electronically addressed light valves the current through the device is modulated spatially.

IV.2. Motivation for Research

There appear to be two major motives for research in photorefractive materials. The first is that one can perform many different optical processing algorithms in these materials with low-power cw lasers, at room temperature, at modest cost, in simple and compact systems, and with a relatively sturdy material. The second motive is that qualitatively new processes appear in experiments that use photorefractive materials because the nonlinearity is so large.

Motivation for research with liquid crystal light valves is clear. These light valves are in commercial production and any improvements in performance or new ways of using them can be translated directly into products.

In a broader sense, the motivation for research in photorefractive materials, light valves, and many other nonlinear materials is provided by a large number of parallel computing applications that either require the manipulation of huge amounts of optical data or require more computing in a shorter time period than can be obtained digitally with current supercomputers. Examples of systems in which photorefractive materials may have realistic near-term applications include real-time optical pattern recognition, real-time command, control, and communication (C^3) optical signal processing, optical computing modules, and the real-time synthetic array radar processor.

IV.3. Review of the Field

Current photorefractive materials consist of electrooptic crystals such as $BaTiO_3$,[1] $KNbO_3$,[2] $LiNbO_3$,[3] $Sr_{1-x}Ba_xNb_2O_6$ (SBN)[4] (ferroelectrics), $Bi_{12}(Si, Ge,Ti)O_{20}$ (nonferroelectric oxides),[5,6] and GaAs,[7,8] InP,[7] CdTe (compound semiconductors). The mobile charge in these materials is provided by a donor (or acceptor) trap system such as provided by iron in two valence states (Fe^{2+} and Fe^{3+}) in $KNbO_3$,[2] $LiNbO_3$,[9] InP,[7] and probably $BaTiO_3$ (Ref. 10) or by the defect EL2 and $EL2^+$ in nominally undoped GaAs.[7]

Photorefractive materials permit construction of unique devices. Optical amplifiers with gain factors of 4000 (Ref. 11) have been constructed using photorefractive materials and cw lasers. Efficient self-pumped conjugators that are self-starting and require no external pump beams have also been constructed using cw lasers.[12,13] Here the only competing technology is stimulated Brillouin scattering conjugators that usually require pulsed lasers with more than a millijoule per pulse.[14]

A wide variety of other prototype operations have been performed in devices constructed from photorefractive materials. These operations include matrix inversion,[15] beam clean-up,[16] beam combining or locking,[17] real-time interferometry, associative memory,[18–20] threshold detection,[21] convolution/correlation,[22] edge enhancement,[23] differentiation/integration, holographic storage,[3] wavelength conversion, optical limiters,[24] incoherent-to-coherent conversion, and beam steering[25] or real-time holographic optical interconnection, imaging of phase objects,[26] and rf signal correlation.[27]

A number of factors appear to be obstructing conversion of these prototype devices into marketable devices. First, not all photorefractive materials have a large enough nonlinearity to perform these operations. Second, commercial availability of materials with large nonlinearities is limited. To be specific, $BaTiO_3$, which is available from one commercial supplier, has been used for many of these experiments. Other materials with large nonlinearities, such as $KNbO_3$, SBN, and other tungsten bronzes, and $KTa_{1-x}Nb_xO_3$ (KTN) are not available commercially with good optical quality. Growth of these crystals of the size and optical quality needed for optical signal processing requires an investment of several years, substantial funding, and talented personnel.

A third factor limiting application is low sensitivity. It requires typically 0.5 J/cm^2 to produce a phase conjugate beam with $BaTiO_3$ using self-pumping. Thus for a moderate input intensity of 1 W/cm^2 the response time is of the order of 0.5 s^{-1}. At this speed photorefractive materials cannot compete with light valves or electronic computers. Finally, available crystals of $BaTiO_3$ are somewhat smaller ($<5 \times 5 \times 5$ mm) than desirable for the typical optical processing algorithms. Other photorefractive materials are faster [e.g., $Bi_{12}SiO_{20}$,[28] or GaAs (Ref. 7)] or available in larger pieces (GaAs, $LiNbO_3$) but none of these is as nonlinear as $BaTiO_3$, and $LiNbO_3$ is slower (see Ref. 29, Table II). Other materials such as semiconductors like CdTe or InP have simply not been the subject of much investigation.

The limits of performance of photorefractive materials can be assessed in a number of ways.

A. Speed

The photorefractive effect is essentially a response to optical energy; refractive-index change per absorbed photon.[30] The effect scales with energy until times as short as either the time for a charge carrier to move one grating period or the time necessary for the electrooptic effect to respond to the Coulomb field of the displaced charge. The longer of these times is the fundamental limit. Diffusion times in semiconductors such as GaAs are known to be <10 ps.[31] The electrooptic response time is of the order of attoseconds for the electronic component of the electrooptic coefficient, r, and picoseconds for the ionic part.[32] The mix of these two components seems to vary from crystal to crystal, but the worst case is again in the picosecond range.

B. Damage

Optical damage thresholds for pulsed radiation are comparable to other optical materials (50–500 MW/cm^2).[33] Many photorefractive crystals are extremely rugged and have a long working life. One researcher reports that his barium titanate crystal has been used many thousands of hours over nine years in argon-ion laser beams (often focused at full power) and doubled Nd:YAG pulsed beams (joules per cm^2 per pulse) with

no sign of deterioration. Other researchers have not been so fortunate, reporting damage from pulsed lasers of 1-W/cm^2 average power and damage from the thermal shock of removing painted electrodes with acetone.

C. Ultimate Size of Nonlinearity

Two approaches have been considered. In the first, the refractive-index change Δn in a photorefractive material is given by $\Delta n = n^3 rE/2$,[30] where n is the background index, r is the electrooptic coefficient, and E is the space charge field. The optimum field that can be obtained is when each absorbed photon separates one charge carrier by a grating period Λ_g: $E = Ne\Lambda_g/(\varepsilon\varepsilon_0)$, where N is the number density of absorbed photons, e is the charge on an electron, ε is the dielectric constant, and ε_0 is the permittivity of free space. The resulting index change per absorbed photon density then depends only on the grating period, the index n, and the ratio r/ε. For typical parameters these considerations yield $\Delta n/N \simeq 10^{-19}$ cm^{-3}. In the second approach, the energy required to obtain a phase conjugate reflectivity per pixel of 100% was calculated. This result again depended only on the ratio r/ε and n and a lower limit of $\sim 10^{-14}$ J was obtained.

A number of significant gaps in current knowledge of photorefractive materials have been identified. First, the microscopic behavior of $BaTiO_3$ is not completely understood.[10,34] This includes factors such as whether one or more species is responsible for the mobile charges, the relative role of electrons and holes,[35,36] a model for the response time,[37] and measurement of the mobility, quantum efficiency, and ionization/recombination cross section. Second, a detailed understanding of the fundamental limits on the ratio r/ε, which control sensitivity, is not available. The ratio r/ε varies by only about an order of magnitude for all known photorefractive materials while r varies from 1 to 2000 pm/V and ε varies from 10 to 4000 (Ref. 27, Table II). Third, what techniques are available for optimizing properties such as quantum efficiency, species densities, cross sections, mobilities?[10,34] Fourth, there are broad gaps in our knowledge of crystal chemistry and crystal growth techniques that directly affect research in photorefractive materials. Finally, are there other photorefractive materials such as organic materials, or materials sensitive in the ultraviolet or far-infrared spectral bands?

D. Liquid Crystal Technology

Liquid crystal (LC) devices are already used for a variety of displays and optical data processing applications in the form of optically or electronically addressed 2-D spatial light modulators. Optical data processing operations performed using liquid crystal devices include the following: image processing operations such as correlation,[38] level slicing,[39] analog to digital conversion,[40] logarithmic filtering,[41] and phase conjugation[42]; signal processing operations such as radar range-Doppler signal processing,[43] feasibility of synthetic aperture radar signal processing,[44] and spectrum analyzers[45]; optical computing operations such as logical functions,[46] binary operations with bistable arrays,[47] and residue arithmetic operations.[48] Finally, optical interconnects using liquid crystal light valves were also demonstrated recently.[49,50] The main merit of LC technology is the extremely high electrooptic coefficient resulting in high resolution, large dynamic range devices. The large spectral bandwidth of liquid crystal is another asset which allows operation ranging from near UV to the IR region.[51] Thus, photoactivated liquid crystal light valves[52,53] are available with resolution exceeding one million elements, dynamic range of >100:1 (or few wavelengths in phase shift), response times of $\simeq$10 ms, and sensitivity of 100 μW/cm^2 for full activation (contrast ratio of 100:1 or refractive-index change of $\simeq$0.1). Electronically addressed devices[54] typically feature $\simeq 300 \times 300$ elements with dynamic range and speed similar to that of the photoactivated devices. It is important to note that photoactivated liquid crystal spatial light modulators (SLMs) perform similar functions to those of photorefractive materials. It is therefore of interest to try to compare their relative performance. Since both classes of device perform an intensity to refractive-index conversion, the photorefractive sensitivity,[55] expressed as the incident energy density required for unity index change, can be used for this comparison. Typical values for photorefractive materials are 1–10^2 cm^2/J.[55] In the case of a typical photoactivated LC-SLM, an index change of $\Delta n \simeq 0.1$ is attained using energy density of 1 μJ/cm^2 (=100 μW/cm^2 at 10-ms rise time). The effective photorefractive sensitivity of a LC-SLM is therefore $\sim 1 \times 10^5$ cm^2/J, which is three orders of magnitude higher than the typical values achieved in photorefractive materials. It should be noted, however, that the resolution of liquid crystal SLMs (typically 10–50 line pairs/mm) is significantly lower than that of the photorefractive effects, which is in the 1000-line pairs/mm regime. If one redefines the photorefractive sensitivity as the incident energy required for a unity change in the refractive index per pixel of information, the above gap in the photorefractive sensitivity between liquid crystal devices and photorefractive materials will shrink considerably. Present efforts are under way to improve the relatively slow response of the nematic materials by using ferroelectric LCs.[56] These can be switched at typical times of 10–100 μs, but are binary in nature. For both classes of material a trade-off exists between the dynamic range and speed of response of the devices, as both quantities are proportional to the thickness of the LC cell.[57] The resolution is presently limited by the driving structure, electronic driving array (CCD-addressed or MOS-matrix), or the photoconductor. Ultimately the resolution will be limited by the fringing field in the liquid crystal layers. Finally, we should mention the large optical nonlinearities which liquid crystals exhibit.[58,59] The molecular reorientation responsible for the large optical modulation is due to either thermal effects or to optically induced fields. Effects such as self-focusing,[60] optical bistability,[61] and wavefront conjugation at a few W/cm^2 (Ref. 62) were recently demonstrated.

IV.4. Conclusions

Expand availability of photorefractive materials. Materials that are known to be interesting for the photorefractive effect such as $KNbO_3$, $Bi_{12}TiO_{20}$, and a variety of mixed crystals ($KTa_{1-x}Nb_xO_3$, $Sr_{1-x}Ba_xNb_2O_6$, $Ba_{1-x}Sr_xTiO_3$, $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$, $Pb_{1-x}Ba_xNb_2O_6$) are unavailable to most researchers. The waiting time to obtain $BaTiO_3$ ranges up to two years.

Encourage (i.e., fund) collaborative research efforts between researchers in crystal growth, in fundamental studies of defects, transport, etc., in development of exploratory devices, and ultimately in development of real systems. The benefits of strong interactions between these four groups have not been realized to a great extent.

Search for and investigate the properties of other photorefractive materials (e.g., semiconductors and organic materials if any are photorefractive). Emphasize molecular engineering of liquid crystals. In particular, this should result in improving the understanding of the relationship between molecular properties (e.g., polarizability) and the macroscopic properties of the LC material (e.g., birefringence). The development of such theory will assist in optimizing LC properties by synthesizing materials according to the guidelines developed by the theory. In particular, one would hope to optimize the dynamic range-speed trade-off in LC materials.

Develop a better understanding of the physics of ferroelectric liquid crystals (FLCs). In particular, use these studies to try to develop a gray-scale operation of FLCs.

Photorefractive and liquid crystal materials have occupied a unique position in research in nonlinear optics for the past ten years. The high nonlinearity that can be obtained in photorefractive materials using low power cw lasers has led to new and unexpected effects and has permitted construction of a wide variety of exploratory devices for optical processing and real-time holography. Key questions for the next ten years concern details of charge transport, achievable speed of response, sensitivity, and crystal availability. New photorefractive materials continue to be identified. In the domain of liquid crystal devices the critical issues are those of optimizing the dynamic range/speed trade-offs through molecular engineering in nematic materials and the development of gray-scale operation in ferroelectric liquid crystals. If these questions can be successfully answered, it seems likely that ten years from now photorefractive and, perhaps even earlier, liquid crystal materials will be used in a wide range of commercial and military products.

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V. Inorganic nonlinear materials for frequency conversion

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V.1. Introduction

Inorganic nonlinear optical materials are used mostly in high-power laser applications for extending the range of wavelengths available at high power. In the past, applications have mostly involved harmonic generation, but recently there has been considerable progress in other types of frequency conversion, such as optical parametric amplifiers. With a single frequency, efficient laser source, these devices promise wide wavelength flexibility at high power and conversion efficiency. As solid state devices they offer some advantages over other options for achieving wavelength flexibility.

The panel believes that these devices have great potential and deserve serious consideration in both military and civilian contexts. Development of a national capability to address our perceived future national requirements a decade from now requires a sustained, cogent national effort in crystal growth and a broad-based systematic materials research program. Because the lead time in this area of research and development program is long, it is important to begin now to have results in the 1990s. The panel believes that applications should provide both impetus and focus for this national effort, but the program should not be devoted totally to applications. The goal is to develop a national capability in this area spanning all its major aspects to meet needs ten years from now.

V.2. Review of the Field

A. Applications

The principal uses of inorganic nonlinear optical materials are:

1. Commercial Lasers

Frequency conversion devices are usually offered as accessories for short-pulse (10-ns) high-power lasers available commercially. These are typically harmonic generators for Nd:YAG lasers. While harmonic generators for other lasers are available, they are not routinely available commercially.

2. Low Average Power Devices

These are miniaturized or portable devices used in information processing, medical instrumentation, xerography, etc.

3. High Average Power Devices

This includes future defense needs in a variety of scenarios, generally summarized as control of high pulse energy, high average power electromagnetic radiation through modulation, deflection, and frequency conversion. Examples include battlefield lasers, submarine communications, countermeasures, and optical radar. A number of industrial processes also require high average power, such as chemical processing, materials processing, and x-ray lithography. The average power required can be up to several kilowatts.

4. Fusion

Because of the high energy per pulse (up to 10 MJ) the primary requirement is for an inexpensive material for frequency conversion to the near UV, with high damage threshold.

B. Materials Requirements

To be useful, it is not sufficient that a nonlinear device work efficiently. The device must also survive

in the operating environment without losing performance over the lifetime of its assignment. Historically, materials scientists working on new nonlinear optical materials have stressed the importance of the optical nonlinearity and have placed less emphasis on other materials properties. For a device to succeed, it is vital that it meet a number of criteria. The panel agreed strongly that these other criteria should receive greater emphasis. The relevant issues include:

For availability:
- reliable crystal growth techniques.

For high conversion efficiency:
- optical nonlinearity;
- birefringence and optical dispersion;
- moderate to high transparency; and
- optical homogeneity.

For ease of fabrication:
- mechanical strength;
- chemical stability; and
- polishing and coating technology.

For high average power:
- low absorption;
- temperature phase matching bandwidth;
- fracture toughness; and
- thermoelastomechanical properties.

For lifetime and system compatibility:
- damage threshold;
- nonlinear absorption;
- nonlinear index; and
- brittleness.

In designing devices, it is essential that the material and the laser be treated together as a system and that any special operating circumstances be taken into account. For lasers in space, for example, vibrations, vacuum, thermal gradients and fluctuations, and remote control are relevant design considerations.

V.3. Current Status

A. Infrared Materials

In the infrared, the available materials are chalcopyrites such as $AgGaS_2$[1] and Ag_6GaSe_2.[2] Other materials such as tellurium,[3] CdSe,[4] Tl_3AsSe_3,[5] and $CdGeAs_2$[6] are also candidates for development. The linear and nonlinear optical properties of these and other nonlinear materials are described in several review articles.[7-11] These materials are all limited in size and optical quality, and a better understanding of chemical phase equilibria is needed for improved growth. Annealing to obtain optical quality is a problem that needs to be addressed. There is also the possibility that materials with synthetically engineered structures can be developed to achieve phase matching.

B. Visible–IR Materials

There is substantial choice for materials in the visible and near infrared, including phosphates, iodates, niobates, and some organic crystals. Among the commonly available materials, potassium dihydrogen phosphate (KDP) and its isomorphs are transparent from the UV to the near IR, and have a threshold power[11] for doubling around 100 MW. They have only a moderate resistance to optical damage, and although they are being considered for fusion the cost for large boules needs to be reduced still further.

Potassium titanate phosphate (KTP) has very attractive properties,[12] including a low threshold power,[11] <100 kW, for doubling Nd:YAG lasers, and a large temperature bandwidth. It is grown by either a hydrothermal or a flux technique, and suffers from inclusions. The largest volume currently available is $\sim 5 \times 5 \times 5$ mm and is extremely costly.

Lithium niobate is noncritically phase matched near 1064 nm but has suffered from a photorefractive damage which has limited the doubling efficiency. New material doped with MgO apparently solves this problem,[13] but it is not commercially available in the United States. It is also one of the most temperature sensitive of all nonlinear materials.

Potassium niobate is potentially very attractive for doubling diode lasers at an efficiency of a few percent.[14] It is not available in the U.S., and obtaining single crystals involves a delicate poling procedure. It is unlikely that the growth technology is scalable beyond $\sim 10 \times 10 \times 10$ mm.

Lithium iodate has a wide range of transparency,[15] and improved crystal growth techniques have led to material sufficiently transparent in the UV to triple 1064 nm efficiently.[16] Its damage threshold is rather low (2–4 J/cm^2 at 1 ns), but it is available in large sizes. It has high birefringence and therefore a high threshold power.[11]

In new materials for this wavelength range, L-arginine phosphate is currently under development.[17] It is easily grown from aqueous solution with high optical quality, has high threshold for optical damage, and is more efficient than KDP. It is being developed as a replacement for KDP in fusion and in doublers for small commercial lasers.

C. UV Materials

There are very few nonlinear materials with attractive properties for generating light below 200 nm. Urea has been studied for several years.[18] It is difficult to grow, and polished surfaces other than cleavage surfaces are extremely hygroscopic. Devices based on urea must immerse the crystal in oil, which is usually absorbing in the UV. Urea has been used in an optical parametric oscillator to generate tunable radiation throughout the visible.[19] A commercial crystal grower is working on urea, but scaling the crystal size is still an issue, and the crystals apparently have strong intrinsic absorption lines, making them unsuitable for work near 1000 nm.

Beta barium borate is a new material developed in the People's Republic of China.[20] Its threshold power for doubling is ~3–4 times higher than KDP, but its temperature bandwidth for doubling 1064 nm is the largest of any known material. It has a high damage threshold, is transparent from 200 to 3000 nm, and is phase matchable for fifth harmonic generation at 212 nm. It is grown from a flux and tends to have inclusions. Considerable effort will be necessary to grow

large transparent crystals. Phase-matched second harmonic generation down to 204.8 nm has recently been achieved in this material.[21] It is a promising material for short-pulse (<1-ns) high-power (1-GW) lasers but is not available in the United States.

Often, the damage threshold and available size of existing nonlinear materials are too small, and their threshold power is too large. Each material has some idiosyncracy which is disadvantageous. It is important to recognize that the problems with these materials are not with their nonlinearity, which has been the primary focus of past thinking. Their faults, if such a term is applicable, lie in other areas, such as linear optical, mechanical, or chemical properties. All of them would benefit from sustained work on their crystal growth. Finally, it is important to match the laser sources used and the material. Materials with low threshold power will be more forgiving of poor beam quality; the comparative lack of low threshold power materials has hindered the development of nonlinear optical devices in the past.

V.4. Conclusions

Work on nonlinear materials for high-power lasers is quite limited in the United States. Groups at Stanford and Cornell are well established and are developing specific materials. A larger group at Livermore has begun a longer term systematic investigation.

One panel member was concerned because most of the new ideas in nonlinear materials appear to originate outside the United States. A partial answer to why this has happened lies in comparing U.S. research and the Chinese group which discovered barium borate. That group consists of nine doctoral level scientists and about the same number of support staff. It involves theoretical modeling, chemical synthesis, crystal growth, and experimental physics. The Chinese group has been working in this area for at least ten years. A similar situation exists in Cologne in West Germany, where Haushuhl's group is engaged in long-term research. In contrast, the United States commitment in this area has been generally intermittent and weak.

Nonlinear optical processes are capable of efficient, scalable frequency conversion at high average power.[22] This includes frequency agile devices such as optical parametric amplifiers which are capable of continuous tuning over a wide frequency spectrum. Solid state nonlinear devices offer many advantages, including compactness, simplicity, and reliability, and they are capable of high efficiency at high average power. Similar advantages are found for electrooptic switches and modulators.

The panel foresees great potential for solid state nonlinear optical and electrooptic devices. It recommends serious consideration of these devices in both military and civilian systems. Specifically, the panel recommends the following long-term program:

(1) A rational, well-thought out program in crystal growth and associated technology. This program would address the crystal growth of specific important nonlinear materials, but would be thoroughly scientific in its approach, so that the experience gained could be transferred to new materials, where appropriate. The program would require sustained funding, of the order of 25–50 million dollars, spread over an initial ten year period. This research cannot be accomplished with small, 100 K$ contracts, administered on a yearly basis.

(2) A systematic approach to the use and performance of nonlinear materials in applications. This requires a program with:

(a) thorough design analysis of their performance;

(b) evaluation of the materials requirements for the various applications listed above, as well as any other more specific devices; and

(c) continued development of expert systems such as the one at Lawrence Livermore National Laboratory to identify candidate materials for each of these applications.

(3) A systematic approach to the search for new materials. This involves:

(a) theoretical modeling of nonlinear susceptibilities, birefringence, and dispersion, and the establishment of structure–property relationships for nonlinear optical materials in general; and

(b) basic experimental research directed toward characterizing and cataloging the linear and nonlinear optical properties of materials to provide data for model development.

Additional recommendations by the panel concerning near-term, high-priority research are:

(1) Target the following materials for crystal growth development and further characterization:

beta barium borate,
potassium niobate,
KTP,
L-arginine phosphate, and
chalcopyrites and Tl_3AsSe_3.

(2) Investigate nonhomogeneous material structures for enhanced nonlinearities and phase matching.

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VI. Organic and polymeric materials

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VI.1. Introduction

There are certain properties of organic materials which make them unique and attractive materials for nonlinear optical purposes. Interest about organics increased subsequent to demonstrations that large nonresonant responses can be found among particular structural classes.[1] Although reports of enhanced resonant nonlinear response in molecular and polymeric materials have begun to appear,[2] the panel decided to give only brief attention to this newer area. Also, although organic in nature, liquid crystals were excluded to the extent that nonlinearities arise from cooperative rather than intrinsic intramolecular reactions to electromagnetic fields. With these restrictions, using the simple perturbative nonlinear susceptibility formalism, a distinction was made between second-order and third-order properties. These were addressed by separate panel subgroups, since, beyond globally common special properties, the materials requirements for nonlinearity as well as the device architectures and related materials needs are different. A third subgroup reviewed these common special properties. The report below begins with the latter, followed by sections on second-order and third-order nonlinearities.

VI.2. Primary Properties

Large nonresonant nonlinear (intramolecular) polarizability has been observed and documented in certain organic materials.[3] Resonant processes have been used in many media to achieve substantial nonlinear behavior, however, in these organic materials the nonresonant responses are unusually large. Normally these responses are a small fraction of the linearly induced charge displacement. The comparatively large associated hyperpolarizabilities in organics are thought to be dominated by electronic motions associated with delocalization. Thus ultrafast, spectrally broadband (nearly flat), enhanced behavior is possible in low-loss regions of the materials' optical spectra. The mechanisms of nonlinear response have been explained with models ranging in complexity from naive simplicity to detailed many-electron computer calculations.[1,3,4] With the diversity of molecular or polymeric structure and composition available through chemical practices, variation of the properties (e.g., state orderings, symmetries, oscillator strengths, dipole moments, excitation energies, dynamical pathways) which enter these models not only enables detailed testing and investigation of nonlinearity mechanisms, but also implicitly underlies the idea that molecular engineering of nonlinear properties is possible. With organic materials there is an extremely high flexibility of material design.

VI.3. Secondary Properties

The magnitude of nonlinearity is an important characteristic, but, as has been well illustrated over the past two decades, other physical and chemical properties, in addition to fabrication limitations, severely restrict the utility of any nonlinear material. A major advantage of organics and polymerics is their extreme diversity of structure and their flexibility in fabrication. Numerous condensed phases occur or are possible with molecular and polymeric media. They can be formed in bulk, as films, in fibers, etc.—all forms useful for guided or free wave optics. Low temperature thermal and chemical/physical processing is common with high throughput and shape or conformation moldability. Materials are integrable. Pattern rendering and metallization are possible, etc.

Some physical properties of organic materials are or might be advantageous in devices. The low density and average atomic number of organics favorably influence device mass and radiation transparency. Refractive indices are universally small even in organic materials with enhanced nonlinearity. Figures of merit can be higher, since larger electric fields and smaller polarization fields accompany optical waves.

The static or low frequency dielectric constant can also be small even in enhanced nonlinearity materials. Thus lower electrical charges are required to drive electroded structures and larger fields will exist within an organic in inhomogeneous electroded structures resulting in larger device figures of merit. The generally smaller magnitude of n reduces reflection loss problems and scattering problems due to fabrication imperfections. On the other hand, large changes in n are achievable, at least in polymers, so that sharper turns, smaller holographic elements, etc. can be created in integrated circuitry. Evanescent-field nonlinearity, waveguide-device architecture is also possible since smaller refractive indices are available for active cladding. Materials with low dielectric constants can be used in longer traveling-wave electroded optical devices due to smaller velocity mismatch between optical and low frequency waves.

Although long-term behavior is not well known and universal applicability is not true, optical damage thresholds can be high (>1 GW/cm^2 with nanosecond pulses).

On the other hand, there are disadvantageous or unknown factors in the utilization of organic and polymeric materials. Optical transmission is limited on the short-wavelength side by the ultraviolet cutoff. Although many colorless materials exist, there is a loose correlation between enhanced nonlinearity and longer-wavelength cutoff. On the long-wavelength side the occurrence of vibrational overtone and combination absorptions is a severe restriction. Because of the low mass of hydrogen atoms, in hydrocarbons substantial absorption (>1 dB/cm) is the rule even to wavelengths as short as 1.1 μm, although chemistry could conceivably overcome this restriction by use of perdeuterated or perfluorinated compounds. Also, associated with the complex vibrational behavior of organics is the possibility that the imaginary part of the low-frequency dielectric constant may be substantial and dispersive, leading to more complicated electronic drive requirements and to large heating effects in (linear) electrooptic devices. It should be noted that the temperature dependence of physical properties is generally large in organic and polymeric materials—a potential problem for phase-type optical devices. Long-term photochemical/photophysical stability of specific materials and structures under intense optical irradiation, as would necessarily exist in guided wave devices, is not known. One might ask whether the occurrence of enhanced nonresonant polarizability might not enhance the probability of multiphoton absorptions and photochemistry.

VI.4. Second-Order Nonlinearity

Second-order response of organic materials arises from microscopically polarizable units. It is beneficial to separately discuss (1) molecular aspects, (2) macroscopic assemblages, and (3) devices.

A. Molecular Aspects

The second-order hyperpolarizability β has been characterized most widely by the dc electric field-induced second harmonic generation liquid method,[1,3] recently second harmonic generation from molecules oriented at surfaces has been utilized.[5] It was shown that components of β can be highly enhanced by virtue of special asymmetric electronic structure.[1] The large nonresonant electronic contribution to β provides extremely fast response. The electronic contribution is fully utilized by and governs totally optical second-order processes. Work on a few molecular crystals has shown the linear electrooptic effect to be dominated also by this contribution.[6] Thus crystals of these molecules should display only weak low-frequency dispersion (important for broadband electrooptic modulation). It should be mentioned that all characterization techniques are inadequate with regard to molecules in that they require use of imprecise models to describe the molecular contributions to the condensed phase macroscopic dielectric behavior and/or they probe only an average of the highly anisotropic nonlinearity.

The enhancement mechanism has been attributed to special asymmetric charge displacement identified with charge transfer processes. Models of varying complexity have been used. Large perturbation calculations using configuration–interaction states from semiempirically parametrized molecular-orbital calculations have been cited as the most accurate.[4a] This approach requires the least *ad hoc* assumptions concerning the nonlinearity mechanisms when considering factors such as dispersion. Less complete models, such as the two-level model, allow one to apply concepts and information from spectroscopy and dye and color chemistry as well as providing a more accessible intuitive picture, but must be restricted *a priori* to effectively 1-D charge transfer dominated compounds. The availability of computers and molecular-orbital programs has fostered a number of programs to predict β nonlinearities and structure–property trends. However, there are few unambiguous, indisputable, experimental documentations of molecular properties in the literature. It is fair to say that, although detailed studies of prototypical compounds have been reported, specific overall molecular design criteria useful to chemists have not yet been developed. Little information is available dealing with the behavior of organometallics, of the consequences of multiple substitutions on the prototype systems, or of the behavior of heterocyclic compounds, etc. This is not to say, though, that identification of numerous nonlinear molecular species is not or has not been possible; but rigor is lacking in discussions of their nonlinearity behavior and origins.

This area needs more documented experimentation and dissemination of structure–property correlations.

B. Macroscopic Assemblages

Fortunately, the molecular picture of dielectric behavior is a functional approximation. This allows the

use of a very simplified picture for analyses of $\chi^{(2)}$.[3,7] Consequently, it is an advantage that the (molecular) unit properties can be tailored. Because of the molecular nature of organic and polymeric materials, low temperature and special unique processing procedures can be employed to develop second-order nonlinear materials or structures. A variety of generic classes are under study: crystals, polymers, liquid-crystalline polymers, and molecular-state films.[3,7]

Unlike the inorganic counterparts, since the enhanced-nonlinearity mechanism for organics may be associated with the Franck-Condon optical transitions and dipole moments involving only a few excited states and the ground state, while on the other hand it is the accumulated effect of such transitions to all excited states which determines the linear polarizability, there is no requirement to have large n to have large purely optical $\chi^{(2)}$ (i.e., enhanced nonlinearity organics are intrinsically exceptions to Miller's delta rule).[8] Similarly, a reliance on ε-enhancing atomic or ionic motions for large nonlinear response is not necessary, as for inorganics, for large linear electrooptic $\chi^{(2)}$ (i.e., enhanced nonlinearity organics are also intrinsically exceptions to the near constancy of the polarization-optic coefficient f).[8] There are clear advantages to this, as mentioned in Sec. VI.3. While several very large nonlinear coefficients for, e.g., second harmonic generation have been reported, leading to high figures of merit, the electrooptic coefficients reported to date are at best only comparable to lesser nonlinear inorganics such as $LiNbO_3$. The additional (ferroelectric) phonon-mechanism, although a disadvantage in some ways (thermal sensitivity near Curie temperatures, large ε *vis-a-vis* figures of merit), causes much larger nonlinear coefficients. Considering the state of $LiNbO_3$ processing for optical communications use, it is clear that organics have far to go to be considered as alternatives let alone as future generation replacements.

A fundamental requirement for second-order nonlinearity is a noncentrosymmetric structure. More importantly, to effectively utilize β, since the largest components tend to be along permanent dipoles μ, polar molecular alignments are needed. This causes a tremendous limitation. For example, there is a loose correlation between magnitudes of β and μ, and given the propensity for antiparallel ordering of large-μ molecules, large-$\chi^{(2)}$ assemblages of large-β molecules are not common. This is an old problem in the field and a number of chemical approaches have been tried to overcome it.[3]

To date, several molecular crystals have been identified which have good nonlinear susceptibilities. Utilization in second harmonic generation and parametric applications is, however, restricted by linear optical properties, i.e., by $\chi^{(1)}$. As mentioned above, there is not necessarily a significant connection between $\chi^{(1)}$ and $\chi^{(2)}$ properties, nor can it be claimed that there is generally a method to actually control or engineer them [e.g., to accurately predict crystal structures for these molecules and to subsequently calculate $\chi^{(1)}$ with high precision]. Consequently, most crystal work has been empirical search and evaluation, with a few prime materials having been identified.[3,9] Major effort was then required to develop purification and crystal growth techniques and to complete the optical characterizations. These growth techniques are not universally transferable between materials, and the crystals may be environmentally sensitive or fragile. Recently interest in microcrystal and/or encapsulated crystal growth has emerged.[10] Growth is quicker and the small dimensions achieved cause waveguide propagation. Phase matching in nonlinear processes in this case becomes a variable function of the macrostructure rather than simply an intrinsic crystal property. As for any waveguide, the intensities can be kept high over longer distances than with freely diffracting propagation in bulk crystals, potentially enabling similar optical conversions at lower powers.

Research on molecular films[11] and polar polymers[3,12] (e.g., orientational electrets) for second-order nonlinearities is very new. There is hope that these noncrystal-based approaches will allow more direct utilization of the molecular nonlinearity. Also, since device fabrication and performance are seriously limited by the format of materials, these approaches have obvious advantages due to their diversity and flexibility. It is quite early in the development of such materials and probably premature for a realistic evaluation of merits.

C. Device Performance

Crystalline organic materials have been grown in laboratories and various sets of physical properties necessary for knowledge of their performance in devices have been measured. A few reports of operation of nonlinear optical conversion devices appear in the literature.[13] These, though, have been laboratory demonstrations. General availability of device quality materials has been very low to people whose expertise is in device performance and engineering so that the real practical advantages and limitations of specific organic materials have not been assessed. The actual building of devices has not been a general priority among scientists studying the origins of nonlinearity, or inventing, or identifying and physically characterizing these materials.

VI.5. Third-Order Nonlinearity

Excluding simple liquid-crystalline media, third-order nonlinearity characterizations have been reported primarily in a few classes of conjugated organic materials: molecular fluids, conjugated polymers, and liquid-crystalline polymers. Third harmonic generation has been used to unambiguously probe the purely electronic response, with systematic empirical study of molecular structure–property relations being in the early stages.[3,7,14] To characterize more scientifically and preparationally complex polymerics the more straightforward nonlinear refractive index and degenerate four-wave mixing techniques have also been employed. However, those responses may include alternative mechanisms and less easily identified resonance

enhancements (two-photon, Raman, orientation-correlation, electrostrictive, and thermal). Maximum nonresonant $\chi^{(3)}$ magnitudes $\simeq 10^{-9}$ esu have been suggested based largely on work in polydiacetylene (PDA) neat materials.[2c,15] This is a subpicosecond responding nonlinearity.[16] Slower nonlinear mechanisms have been observed to be dominant in solutions of PDAs and in other conjugated polymers. If one includes a less restrictive set of organics (liquid crystalline and colloidal/suspension media), much larger and slower nonlinearities occur. Because of this, a crudely universal nonlinearity relaxation time product has been suggested. While the rapid electronic response in conjugated polymers occurs above the norm, it is at present uncertain what the general limits are and whether the special properties of organics and polymerics will counterbalance the device design constraints of lower, but faster, nonlinearity.

Theory of the origin of the rapid, electronic, enhanced nonlinearity has developed using simple pi-electron theories (particle in box and Huckel theory) with more complete and complex, many-electron computer calculations subsequently being adopted.[1,4] In all cases, delocalization of pi-electrons is the cited source of enhancement. However, the accurate inclusion of correlation effects is known to be important in many 1-D systems, raising doubts about some computations of nonresonant nonlinear behavior. While conjugated polymers have been the universal arena of interest, recently it has been suggested, subsequent to analysis of the nonlinear microscopic dielectric relationships and analysis of errors in nominally third-order nonlinear optical experiments, that cascading of the better understood second-order nonlinearities through local and macroscopic electric fields can lead to comparably large third-order responses.[8]

Among conjugated polymers there is a broad choice of crystalline, liquid-crystalline, and amorphous materials. Growth and fabrication of thin optical-quality films and crystals of specific materials have been demonstrated. Since new techniques (e.g., shear-induced crystallization and solubilization by doping or chemical modification) have recently made some of these possible, it is likely that others will follow.[17]

Limitations on the practical use of organic and polymeric materials include the size of nonresonant $\chi^{(3)}$, as stated above, the situation that materials are not widely available, and consequently the limited experience in growth and fabrication of conjugated polymeric materials into optical devices and in the characterizations of these devices.

Potential applications include optical processing (switching, modulation, logic) in various formats which amplify the consequences of $\chi^{(3)}$ (waveguides, etalons), phase conjugation, and related image processing techniques.

Several needs and trends are seen in the future: broader theory, coupled to experiment, to obtain microscopic and macroscopic models of third-order nonlinearity including electron correlations; larger experimental data base for the latter and for improved understanding of the origins of $\chi^{(3)}$, specifically resonant and nonresonant measurements on prototype systems and additional excited state spectroscopic measurements to understand level structures and dynamics; development of growth and fabrication techniques for prototype devices; stronger links with synthetic organic and polymer chemistry to expand concepts and develop novel materials; availability of materials to the general optics community for familiarization and identification of important properties.

VI.6. Conclusions

There is limited fundamental knowledge to deal with a number of issues in condensed-phase molecular behavior which (1) are associated with our understanding of the behavior in relation to and (2) which affect our ability to develop new materials and improve older ones for nonlinear optical applications. These include a theoretical formalism for off-site intermolecular interactions and orientational distribution functions to predict assemblies, macroscopic structures, and condensed phases; understanding of material pattern formations at intermediate length scales (i.e., 10^2–10^4 Å) which lead to complex birefringence patterns and scattering; anisotropy of nonlinear response; realistic treatment of the microscopic local field and distributed polarizability problems; resonant responses and processes; dynamics theories and experiments, structure–property relationships.

The field of organic and polymeric nonlinear optical materials is still only minimally developed. There are wide gaps in our knowledge of structure–property relations and our ability to make the best choices of materials. Funding of high quality scientific research is essential. Beyond this, further scouting and inventing of new materials and types of molecular assemblies are needed. Emphasis should be given to fabrication characteristics. Furthermore, since the external community is anxious to use new materials and since materials investigators could benefit from feedback concerning auxiliary properties (e.g., optical damage, thermal sensitivities, aging, and other unexpected factors) but typically do not have resources or freedom to produce optimized material for them, it is strongly recommended that either centers or funding for independent contracting to provide usable optical device quality quantities of known nonlinear organics be made available.

VI.7. References

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VII. Limits on nonlinear optical interactions

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VII.1. Introduction

For nonlinear optical interactions, constraints imposed by electrodynamics and materials parameters limit applications. Some of these limits are fundamental in character, depending, for example, on the characteristics of the energy levels involved; i.e., on the matrix elements of transitions which give rise to the nonlinearity. Others do not depend on basic parameters and can be manipulated to optimize particular interactions. Examples of these include the utilization of resonant enhancement to increase a nonlinearity at the expense of increased loss or decreased coherence length, or the manipulation of densities of states to increase nonlinearity in specific spectral regions at the expense of nonlinearity in other regions. Many nonlinear optical applications will depend on these parameter trade-offs.

Predicting the ultimate limits is important both intrinsically and as a basis for comparison with real materials. An example of an estimate of limits is the switching energy associated with an absorptive transition, as discussed below. Whether ultimate limits can be achieved in realistic systems depends on the particular application of interest and the ability to discover and develop material systems and device structures which approach these limits.

VII.2. Constraints on the Applications of Nonlinear Optical Materials

The determination of ultimate performance figures for nonlinear optical materials depends strongly on the specific application for which the material is intended. It is clear that the material requirements are widely different for diverse applications such as optical logic, optical signal processing, optical switching, optical memories, modulation, and frequency conversion. In addition to the nonlinear properties, the linear optical properties as well as the mechanical and thermal properties and chemical stability must also be taken into account. The optimization of specific performance figures is also important, e.g., is speed more important than sensitivity. The ability to process the material and produce specific geometric configurations, such as thin films and fibers, is also a factor.

Basic nonlinear optical interactions can be divided into two categories depending on whether the application requires transparency of one or more of the optical signals. For example, in the case of optical modula-

tion, it is clearly important that the signal beam be transmitted with good efficiency. The same is true for harmonic generation and up or down frequency conversion. On the other hand, total absorption of a pump beam can often be tolerated in applications such as optical logic and digital processing. The division into dissipative and nondissipative mechanisms is an important distinction since dissipative interactions can have strong resonant enhancements relative to nondissipative mechanisms and generally give stronger nonlinearities. In the case of dissipative mechanisms, a further distinction can be made depending on whether only bound states are involved in the interaction or free states are permitted. In the latter case, the drift of free electrons as in the photorefractive effect can produce very large effective dipole moments.

The improvement in sensitivity due to the use of resonant enhancement and/or free electron states is usually accompanied by a compromise which results in a loss of speed. In the case of nondissipative interactions involving only virtual electron transitions, the speeds can be exceedingly fast (approximately the time of 1-Bohr orbit or 10^{-15} s). When resonant interactions are employed, however, real transitions occur and the lifetimes of excited states are the determining factors. If free electrons are involved, the drift times can be very long.

When electronic states are strongly coupled to vibrational modes, the speed of resonant interactions is further affected by the conformational dynamics of the system. For example, in the case of the electrooptic effect, the coupling to ionic displacements can limit the speed of response due to the sluggish motion of the large ionic mass.[1]

VII.3. Resonant Optical Nonlinearities

Resonant interaction of light with matter is one of the most efficient mechanisms of formation of a nonlinear refractive index[2-4] which, in turn, is the underlying phenomenon for applications such as optical switching and bistability,[5] four-wave mixing and phase conjugation,[3,4] self-focusing,[6] self-bending, etc. Indeed, ultrastrong nonlinear refractive indices produced in metallic vapors[7] (e.g., D-line resonances in sodium), in organic molecules such as dyes[8] and in semiconductors using excitons[9] are in fact due to resonant interactions. The basic model which describes fairly well most of these interactions is that of the two-level system.[2-4,10] Using, as an example, optical logic,[5] the fundamental aspects pertinent to this model become important in assessment of limits imposed on such important factors as maximum nonlinearity, minimum power and energy required for switching, minimum switching, and relaxation times, etc.

A few problems and issues arise which are of apparent interest and importance.

(1) What are the maximum nonlinear dipole moments which can be achieved in various materials or systems? How are large dipole moments obtained? Are long molecules with inner traps a good idea? Or metallic needles immersed in dielectric medium? Or multiple quantum needles?

(2) What are the optimal dipole moments required to achieve maximum nonlinearity (e.g., maximum possible change of refractive index)? Minimum saturation intensity? Minimum switching energy (i.e., product of saturation intensity and switching time or relaxation time)?

(3) What is the maximum number density of two-level particles? How does this density affect other optical parameters such as the linear refractive index? How appropriate are the Clausius-Mossotti relations for materials with very high refractive indices? Is a new approach required to describe micro- and macro-electrodynamics in highly nonlinear systems with large refractive indices?

(4) By developing molecules or excitons with large dipole moment, systems are created which can be highly anisotropic (both linearly and nonlinearly). Are there any new aspects in the theory of third-order nonlinear tensors for such materials?

(5) With large changes in nonlinear refractive index, what changes may occur in processes such as self-focusing, self-bending? Would it be feasible to obtain stable self-trapping with a cross section smaller than λ^2? Or self-bending with deflection angles $>90°$?

(6) What are the limits of the two-level model itself when the dipole moment increases? Do multipole interactions become important? Would it be beneficial to enhance multipole interactions and use them for nonlinear optical processes? Are there any other factors limiting the two-level model?

(7) Can multilevel transitions substantially enhance the refractive index at one frequency caused by a strong signal at another frequency (light-by-light modulation and control)? What are the optimal conditions for such cross modulation and control? What are the optimal materials and frequencies?

(8) Is it possible, using multilevel (or infinite-level) systems having quasi-equidistant spacings (e.g., a slightly anharmonic oscillator), to obtain very large enhancements on nonlinearities? The enhancement in this case arises from the fact that the dipole moment increases with excitation while relaxation rates do not change significantly. This property of multilevel systems with nearly equidistant spacings is opposite that of two-level systems where an increase in dipole moment is accompanied by a corresponding decrease in relaxation time. What are the candidate nonlinear systems for such a highly nonlinear effect; can we use molecular vibration and rotation in the infrared and submillimeter regions?

It is well known[11] that a driven classical anharmonic oscillator can exhibit hysteretic jumps and, therefore, bistability. Recently it was predicted[12] that even slight relativistic changes in mass ($<10^{-11}$ J) of a cyclotron electron can result in large hysteretic jumps and bistability when the electron is driven by a very weak electromagnetic wave ($<10^{-9}$ V/cm). Recently, this effect has been observed experimentally[13] and multiphoton effects have been proposed.[14] This process may have potential for use in practical nonlinear opti-

cal devices. Some advantages and research questions concerning hysteretic nonlinearities are:

(1) These are the only known systems capable of bistability without feedback, resonators, retroreflection, etc. They represent the ultimate in single particle systems for signal processing applications. Questions arise concerning the feasibility for practical use, the quantum mechanical restrictions imposed on such systems, and the appropriate theoretical model for fast multilevel transitions.

(2) It may be possible to use free electrons in dilute plasmas to obtain the same effect. An analysis needs to be made of the requirements imposed on temperature, density, and volume of the plasma in order to achieve switching.

(3) In narrow gap semiconductors, such as InSb and HgTe, the conduction band is strongly nonparabolic giving rise to an energy dependent effective mass. There are two significant advantages of this nonparabolicity effect compared with relativistic mass effects: the nonlinearity is much stronger, and the effective mass of the electrons is much smaller. With currently available magnetic fields, resonances can be obtained between 5 and 100 μm and the questions arises as to the feasibility of obtaining these anharmonic resonances, together with hysteresis and bistability.

(4) By using free electrons (in Penning traps), plasmas, or conduction electrons in semiconductors together with two frequency pump illumination, strong difference frequency radiation should be observable. It may be possible to obtain useful far-infrared output with this technique.

(5) By pumping with a single frequency laser, high-order subharmonics can be excited resulting in low frequency output which is correlated with the pump. These subharmonics may be useful as links between lasers and atomic clocks in the microwave region.

VII.4. Limits on Resonant Optical Nonlinearities for Switching

Nonlinear optical devices for switching are constrained by the size of the nonlinearity, the speed of material response, and other parameters.[15-18] Speed of response and hence the switching time is determined by the time to reach steady state both when the field is applied and when it is removed. These constraints will be examined for a two-level system, a system which is easy to model and which on resonance or near resonance provides its maximum response. For a two-level system very near resonance, the intensity required to saturate (equalize populations) is inversely proportional to the transition dipole squared and inversely proportional to the product of the longitudinal and transverse relaxation times. Naively, one might think that to lower the saturation intensity one has merely to increase the dipole moment. This will work as long as the relaxation rate is dominated by nonradiative processes. However, as the dipole is increased eventually the relaxation processes will become radiative. If $T_1 > T_2$, the saturation intensity becomes independent of the dipole moment when $T_1 = T_r$, the radiative lifetime, since T_r is inversely proportional to the dipole moment squared. When T_2 also becomes radiative, the saturation intensity becomes proportional to the dipole moment squared, so increasing the transition dipole will cause the saturation intensity to increase. It is also obvious that the saturation intensity will have minimum value when both the longitudinal and transverse relaxation times are radiative and will be further minimized if T_r is chosen to be the desired response time. Note that the saturation energy flux is also minimized, however, it does not depend on the dipole moment. Clearly, it is best to minimize saturation intensity, hence we want to choose the smallest dipole consistent with the required response time. From the required response time and wavelength the dipole moment and saturation intensity can be computed, using the standard expressions for radiative rate and saturation intensity. The saturation power and saturation energy can then be obtained by assuming focusing to an area of a square wavelength. Table I gives expressions for the saturation intensity, saturation power and saturation energy, dipole moment, and absorption length. Table II gives the numerical values of these parameters for some typical wavelength values assuming a 1-ps response time. It is clear that the saturation intensity, power, and energy are minimized by operating at long wavelength while the dipole moment is minimized at short wavelengths.

Some care must be given to justifying certain of the assumptions that have been made. We have allowed the dipole moment to take on values much larger than normal in the visible and very much larger than normal in the millimeter regions. If such dipoles are impractical, either longer switching times or shorter wavelengths must be used; however it is necessary to use larger energies. There is an implicit assumption that the radiation field modes for spontaneous emission are not restricted in any way; this may not be the case if spatial constraints are placed on the radiation field or if radiation trapping occurs. Clearly for optical logic, transit time effects and heat dissipation are also potential limitations. To avoid transit time effects, elements must be smaller in size than $T_r c/n$ and must be

Table I. Radiatively Dominated Process

Saturation intensity	$I_s = (4\pi\lambda^{-2})h\nu T_r^{-1}$
Saturation power (focal area = λ^2)	$P_s = 4\pi h\nu T_r^{-1}$
Saturation energy	$E_s = 4\pi h\nu$
Transition dipole moment	$\mu_{ij} = e\lambda(3/8\pi\alpha)^{1/2}(\lambda/cT_r)^{1/2}$
Absorption length	$L_a = 4\pi/N\lambda^2$

Note that α is the fine structure constant.

Table II. Wavelength Dependence for Picosecond Absorptive Nonlinearity

λ (μm)	10^3	10	1	0.1
I_s (W/cm^2)	2×10^{-7}	0.2	2×10^{2}	2×10^{5}
P_s (W)	2×10^{-9}	2×10^{-7}	2×10^{-6}	2×10^{-5}
E_s (J)	2×10^{-21}	2×10^{-19}	2×10^{-18}	2×10^{-17}
r_d (μm)	8×10^{3}	8	0.24	0.008

consistent with the element size which is dictated by the nonlinear interaction. Heat dissipation must also be consistent with element size and switching energies.

VII.5. Materials for Optical Parametric Processes

Consider the second-order nonlinear optical process. The nonlinear susceptibility $\chi^{(2)}$ is related to the nonlinear polarizability $\alpha^{(2)}$ by

$$\chi^{(2)} = N\langle\alpha^{(2)}(\omega=\omega_1+\omega_2)\rangle[\varepsilon(\omega)+2][\varepsilon(\omega_1)+2]\times[\varepsilon(\omega_2)+2]/3^3,$$

where $\langle\ \rangle$ indicates the average over molecular orientations and the factors $(\varepsilon+2)/3$ are the local field corrections.[2,4] To maximize $\chi^{(2)}$ we need perfect orientation of the molecules. The microscopic expression of $\alpha^{(2)}$ takes the form

$$\alpha^{(2)}(\omega=\omega_1+\omega_2)=(e^3/h^2)\Sigma[\langle g|r|n\rangle\langle n|r|n'\rangle\langle n'|r|g\rangle\times(\omega_1-\omega_{ng}+i\Gamma_{ng})^{-1}(\omega-\omega_{n'g}+i\Gamma_{n'g})^{-1}+\ldots]\rho_{gg}^{(0)}.$$

It is clear that for large $\alpha^{(2)}$ we need large matrix elements of r and small frequency denominators. Resonance with a large density of states could also help.

To have some feeling for the order of magnitude of $\alpha^{(2)}$, let us assume, away from resonance, $|\omega_i-\omega_{mn}|\simeq 10^{15}\ \mathrm{s}^{-1}$ and $|\langle m|r|n\rangle|\simeq 0.1$ nm (or $\langle g|r^3|g\rangle\simeq 10^{-24}\ \mathrm{cm}^3$). We then find $\alpha^{(2)}\simeq 10^{-28}$ esu. For large $\alpha^{(2)}$, we must have large $|\langle m|r|n\rangle|$ and small $|\omega_i-\omega_{mn}+i\Gamma_{mn}|$. A large $|\langle m|r|n\rangle|$ requires extended overlapping wave functions of both $\langle m|$ and $\langle n|$. One question which arises concerns the upper limit on the value of $|\langle m|r|n\rangle|$. How small $|\omega_i-\omega_{mn}+i\Gamma_{mn}|$ can be depends in practice on how much absorption the particular application can tolerate. The limiting value of $|\omega_i-\omega_{mn}+i\Gamma_{mn}|$ is Γ_{mn}, which is governed by the damping mechanism. The smallest Γ_{mn} a system can have arises when spontaneous emission appears to be the only damping mechanism. In this case, Γ_{mn} is directly related to the matrix element $\langle n|r|m\rangle$, as has been discussed above for a two-level system. Thus, we recognize that the matrix elements are the most fundamental quantities in this discussion. For large $\alpha^{(2)}$ near resonance, one would also like to have as many resonant states as possible. The ideal case would be that the system has only two sets of degenerate states, forming a two-level system. In real cases, one may manipulate the material structure (such as reducing the effective dimensionality) to increase the density of states in narrow frequency regions.

As another example, we consider the third-order polarizability

$$\alpha^{(3)}(\omega=\omega+\omega-\omega)=(e^4/h^3)\times\Sigma[\langle g|r|n\rangle\langle n|r|n'\rangle\langle n'|r|n''\rangle\langle n''|r|g\rangle\times(\omega-\omega_{ng}+i\Gamma_{ng})^{-1}(\omega_{n'g}+i\Gamma_{n'g})^{-1}(\omega_{n''g}+i\Gamma_{n''g})^{-1}+\ldots]\rho_{gg}^{(0)}$$

Letting $|\langle m|r|n\rangle|\simeq 0.1$ nm, $\omega_{n'g}=0$, $\Gamma_{n'g}\simeq 10^{10}\ \mathrm{s}^{-1}$, and $|\omega-\omega_{ng}+i\Gamma_{ng}|\simeq 10^{15}\ \mathrm{s}^{-1}$, we find $\alpha^{(3)}\simeq 10^{-28}$ esu, corresponding to $\chi^{(3)}\simeq 10^{-5}$ esu for $N\simeq 10^{22}\ \mathrm{cm}^{-3}$. Here, because of the resonance with $\omega-\omega-\omega_{n'g}\simeq 0$, $\alpha^{(3)}$ is enhanced, but then the relaxation time of $\alpha^{(3)}$ is correspondingly reduced and limited by $\Gamma_{n'g}^{-1}$. The value of $\alpha^{(3)}$ can be further enhanced by moving ω toward ω_{ng}. At $|\omega-\omega_{ng}+i\Gamma_{ng}|\simeq 10^{13}\ \mathrm{s}^{-1}$, we have $\alpha^{(3)}\simeq 10^{-24}$ esu and $\chi^{(3)}\simeq 10^{-1}$ esu. Bringing ω even closer to resonance will invalidate the perturbation calculation that leads to the above expression of $\alpha^{(3)}$. Saturation pumping comes in and it is now more appropriate to discuss the problem using the model of an effective two-level system.

VII.6. Conclusions

The significance of fundamental limitations will increase as applications progress and as optical technologies become able to compete more effectively with other technologies and become more sophisticated in character. The demand for researchers with firm knowledge in both fundamental and practical areas of optical technology will increase and broaden in the future. Achieving the fundamental limits will entail increased sophistication, cost, and complexity of nonlinear optical materials research and nonlinear optical device fabrication.

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