

## Fundamentals of nonlinear optical materials

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**Abstract.** In this article, we briefly review the fundamental aspects of nonlinear optical materials and their role in modern communication.

**Keywords.** Nonlinear optics; nonlinear polarization; optical fiber communication; optical switching.

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### 1. Introduction

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. The new development of techniques for the fabrication and growth of artificial materials has dramatically contributed to this evolution. The aim is to develop materials presenting large nonlinearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response, and high damage threshold. But in addition to the processability, adaptability and interfacing with other materials improvements in nonlinear effects in devices, led the way to the study of new NLO effects and the introduction of new concepts. Optical solitons, optical switching and memory by NLO effects, which depend on light intensity, are expected to result in the realization of pivotal optical devices in optical fibre communication (OFC) and optical computing which make the maximum use of light characteristics such as parallel and spatial processing capabilities and high speed.

Some materials change light passing through them, depending upon orientation, temperature, light wavelength etc. (red light, lower wavelength) releasing one photon of accumulated higher energy (blue and green light, higher wavelength). NLO materials typically have a distinct crystal structure, which is anisotropic with respect to electromagnetic radiation. The importance of nonlinear optics is to understand the nonlinear behavior in the induced polarization and to analyze and to control its impact on the propagation of light in the matter. The NLO phenomena can be represented by the Maxwell equations

$$\begin{aligned}
\underline{\nabla} \wedge \underline{E} &= -\frac{\partial \underline{B}}{\partial t} \\
\underline{\nabla} \cdot \underline{E} &= \rho \\
\underline{\nabla} \wedge \underline{H} &= \underline{J} + \frac{\partial \underline{D}}{\partial t} \\
\underline{\nabla} \cdot \underline{B} &= 0
\end{aligned} \tag{1}$$

with  $\underline{D} = \underline{E} + \underline{P}_L + \underline{P}_{NL}$ , where  $\underline{P}_L$  is the linear polarization and  $\underline{P}_{NL}$  is the nonlinear polarization. Nonlinear optics is used either to shift the optical frequency of the available fields or to remodel their spatiotemporal characteristics. Accordingly one can separate the nonlinear effects into two classes. One class encompasses those which serve to generate fields at new frequencies in which case the coherence or equivalent to the field amplitude matters and one is invariably faced with the problem of phase matching conditions. The example here is the second harmonic generation (SHG). The frequency preserving effects like the optical Kerr effect can be used for bistable operation, phase conjugation, soliton formation and other operations on the spatiotemporal profile of coherent light pulses: here one can also include the hybrid effects like electro-optic, magneto-optic and acousto-optic effects that can be used for parametric devices. The other class includes effects where one modifies the spatiotemporal characteristics of a light beam, in particular the spatiotemporal profile and polarization state, without touching its carrier frequency, in which case the phase matching condition is practically absent. Here, one has either the high self-effects or photo-induced ones where only the spatiotemporal profile of the beam matters and not the field amplitude. The frequency shifting effects like the sum or difference frequency generation processes, allow one to convert up/down the frequencies of the existing light sources. Examples are the optical nonlinearity mediated effects or the parametric effects where an external parameter is used to modulate the optical characteristics of the medium, the classic examples here being the electro-optic (Pockel's) and acousto-optic effects.

The enhancement of the efficiency of the nonlinear process by the appropriate choice of NLO material interaction configurations constitutes a central concern in all these studies. The development of nonlinear optics is intimately connected with progress in NLO materials. An NLO material is a compound in which a nonlinear polarization is invoked on application of an intense electric field. This electric field results from the external application of an intense laser-source. Mathematically, the NLO effect can be described on the molecular scale by the following total polarization:

$$P_{\text{TOT}} = m + \epsilon_0(\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots), \tag{2}$$

where  $P_{\text{TOT}}$  = the total polarization of the molecule;  $m$  = the permanent dipole moment;  $E$  = the electric field;  $\chi^{(1)}$  = the linear polarizability;  $\chi^{(2)}, \chi^{(3)}, \dots$  = the first, second, ... hyperpolarizability coefficients. The most important term is the quadratic and the related phenomenon is known as second harmonic generation (SHG). This is essentially a frequency-doubling process: two waves, each of frequency  $\omega$ , simultaneously superimpose constructively. The resulting wave excites an electron from the ground state to a virtual excited state. On relaxation, one wave of frequency  $2\omega$  is emitted. In order to optimize the SHG effect on a molecular scale, one must optimize  $\chi^{(2)}$ . Various structural features of compounds have been found to influence the value of  $\chi^{(2)}$ . Crystallographically, the compound must be non-centrosymmetric by nature, SHG being an even (second) order tensorial effect.

## 2. Second order effects

In addition to SHG, second order nonlinearity  $\chi^{\leftrightarrow(2)}$  contributes to many interesting effects like optical rectification, linear electro-optic effect (LEO), parametric oscillation and sum and difference frequency mixing. The second order polarization  $\vec{P}^{(2)}$ , which is the source of such nonlinearities, can be given as,

$$\vec{P}^{(2)}(\omega_3) = \chi^{\leftrightarrow(2)}(-\omega_3; \omega_1, \omega_2) : \vec{E}^{\omega_1} \vec{E}^{\omega_2}, \quad (3)$$

where  $\vec{E}^{\omega_i}$  is the amplitude of the field at frequency  $\omega_i$ .

When  $\omega_3 = \omega_2 = \omega$  and,  $\omega_1 = 2\omega$ , the polarization,  $P(\omega_3 = 2\omega)$ , is the source of second harmonic generation (SHG). This effect was first observed by Franken and his co-workers [1], by focussing the 694.3 nm output from a ruby laser onto a quartz crystal and obtaining a very low intensity output at a wavelength of 347.15 nm. Thus the frequency of the incident light gets doubled which enables one to extend the range of laser wavelengths into the blue and ultraviolet parts of the spectrum. One important application from SHG is the laser induced nuclear fusion which appears to be more efficient at higher optical frequencies. In recent years, several papers have reported the occurrence of solitons with SHG.

When  $\omega_3 = 0$ , the effect is called optical rectification. These two results are special cases of the process known as sum and difference frequency mixing of the general cases where

$$\omega_3 = \omega_1 + \omega_2. \quad (4)$$

The left hand side in eq. (4) represents the case of odd-numbered coherence lengths and right hand side in even-numbered ones. If the frequency  $\omega_3$  alone is applied, then the two smaller frequencies can build up from noise where  $\omega_1$  and  $\omega_2$  are known as 'signal' and 'idler' frequencies respectively. A special case that has found many applications is  $\omega_1 = 0$  and  $\omega_3 = \omega_2 = \omega$ , in which case,

$$\vec{P}^{(2)}(\omega) = \chi^{\leftrightarrow(2)}(-\omega; 0, \omega) : \vec{E}^0 \vec{E}^\omega, \quad (5)$$

which is the LEO effect or the Pockel's effect. In this effect, the dc field can be thought of as changing the linear optical susceptibility of the material so that the optical field's propagation parameters are changed by the voltage. Although the input frequency is not modified, the amplitude and phase of the field depend linearly on the magnitude of the dc field.

It can be seen from eq. (4) that if  $\omega_3$  and  $\omega_1$  are fixed, then  $\omega_2$  is also fixed. However, if only  $\omega_3$  is fixed, then the other two are free to range over many values; this effect is known as parametric amplification which is used to produce coherent radiation at frequencies in the ultraviolet region [2,3]. The additional wavelengths made available by harmonic generation and parametric oscillation lead to applications in photochemistry, high resolution spectroscopy, and the remote detection and the identification of atmospheric pollutants by optical radar [4].

### 3. Third order effects

When a medium is centro-symmetric, second order effects get cancelled and third order effects like third harmonic generation, electrochromism and Kerr effect dominate the electromagnetic wave propagation. The susceptibility tensor  $\chi^{\leftrightarrow(3)}$  is responsible for these effects which are not much pronounced unless the optical intensity is very high. In general, it takes interaction of four waves to effect a third order effect [5-7]. The effect of four-wave mixing can be understood by considering the third order polarization term

$$\vec{P}^{(3)} = \epsilon_0 \chi^{\leftrightarrow(3)} :EEE \quad (6)$$

Considering four optical waves oscillating at frequencies  $\omega_1, \omega_2, \omega_3,$  and  $\omega_4,$  and linearly polarized along the same axis  $x,$  the total electric field can be written as

$$\vec{E} = \hat{x} \frac{1}{2} \sum_{j=1}^4 E_j \exp[i(k_j z - \omega_j t)] + \text{c.c.}, \quad (7)$$

where  $k_j = n_j \omega_j / c,$   $n_j$  is the refractive index and all the four waves are assumed to be propagating in the  $z$  direction. Substituting eq. (7) in eq. (6), one can obtain

$$\vec{P}^{(3)} = \hat{x} \frac{1}{2} \sum_{j=1}^4 P_j \exp[i(k_j z - \omega_j t)] + \text{c.c.} \quad (8)$$

$P_j$  ( $j = 1, 2, 3, 4$ ) consists of a large number of terms involving the products of three electric fields. For example,  $P_4$  can be expressed as:

$$P_4 = \frac{3\epsilon_0}{4} \chi_{xxxx}^{(3)} \{ [|E_4|^2 + 2(|E_1|^2 + |E_2|^2 + |E_3|^2)] E_4 + 2E_1 E_2 E_3 \exp(i\theta_+) + 2E_1 E_2 E_3^* \exp(i\theta_-) + \dots \} \quad (9)$$

where

$$\begin{aligned} \theta_+ &= (k_1 + k_2 + k_3 - k_4)z - (\omega_1 + \omega_2 + \omega_3 - \omega_4)t, \text{ and} \\ \theta_- &= (k_1 + k_2 - k_3 - k_4)z - (\omega_1 + \omega_2 - \omega_3 - \omega_4)t. \end{aligned} \quad (10)$$

The term proportional to  $E_4$  in eq. (9) is responsible for self phase modulation and cross phase modulation. The remaining terms are responsible for four-wave mixing. These effects become observable only under the condition of phase matching which means the matching of frequencies as well of the wave vectors. Unlike this, stimulated inelastic scattering processes, which are also third order effects, do not need the requirement of phase matching.

There are two types of four-wave mixing terms in eq. (9). The second term on the right-hand side corresponds to the case in which three photons transfer their energy to a single photon at the frequency  $\omega_4 = \omega_1 + \omega_2 + \omega_3.$  This term is responsible for the phenomena such as third harmonic generation when  $\omega_1 = \omega_2 = \omega_3,$  or frequency conversion to the wave at  $2\omega_1 + \omega_3$  when  $\omega_1 = \omega_2 \neq \omega_3.$  The last term in eq. (9) corresponds to the case in which two photons at frequencies  $\omega_1$  and  $\omega_2$  are annihilated with simultaneous creation

of two photons at frequencies  $\omega_3$  and  $\omega_4$  such that  $\omega_3 + \omega_4 = \omega_1 + \omega_2$ . It is relatively easy to obtain the phase matching condition for this case when  $\omega_1 = \omega_2$  [8,9]. Physically, it manifests in a way similar to stimulated Raman scattering. A strong pump wave at  $\omega_1$  creates two side bands located symmetrically at the frequencies  $\omega_3$  and  $\omega_4$ . The partially degenerate four-wave mixing was originally called as three-wave mixing as only three distinct frequencies are involved [8].

An important application of four-wave mixing is that of squeezing in optical fibers [10,11]. The term squeezing refers to the generation of special states of electromagnetic fields in which noises are reduced to that below the quantum noise level. This is in accordance with the Heisenberg's uncertainty principle that limits the accuracy of observation of two conjugate variables, yet an increase in one variable would result in the decrease of its conjugate variable. From a physical standpoint, squeezing can be understood as deamplification of signal and idler waves for certain values of the relative phase between the two waves [12]. Four-wave mixing is also used for parametric amplification [13]. The parametric gain can be used to make a laser by placing the fiber inside a Fabry-Perot cavity. Such a parametric laser, known as four-photon fiber laser, emits 1.15  $\mu\text{m}$  pulses of 65 ps duration [14].

#### **4. Parametric processes**

In the previously discussed NLO effects the frequencies of the interacting fields were tacitly assumed to be comparable: all fall within the same transparency region of the medium so that all the fields couple to the same degrees of freedom of the medium. The transparency region extends above the vibrational frequencies and below the onset of electronic transitions, as, the valence electrons contribute only to the optical nonlinearities and their response can be assumed practically instantaneous.

If any of the frequencies however is lowered into a different transparency region then the corresponding field couples with additional or even different degrees of freedom. For instance, for frequencies below the vibrational frequencies the ionic motion and its coupling with the electrons set up additional mechanisms for nonlinear polarization as also does the molecular reorientation: these additional mechanisms besides changing the magnitude and even the sign of the nonlinear coefficients may modify some of their symmetry properties, like the breaking down of the Kleinmann symmetry relations and also introduction of different time constants which can be quite crucial when considering very short light pulse interactions. When any of the frequencies lie much higher than the electronic transitions, transparency falls in the X-ray region and the electrons essentially respond as free and the dipole approximately breaks down and the symmetry properties as well subject to approximation, the most conspicuous being  $\chi^{(2n)} \equiv 0$  for media with inversion symmetry. Actually, the multipolar expansion must be abandoned and one must proceed from microscopic Maxwell-Lorentz equations without introducing the space and time average that leads to the macroscopic equations: the relevant quantity now is the microscopic electron density and current distribution.

For such cases where fields of widely different frequencies are interacting, it is more convenient to treat differently high and low frequencies fields and regard the latter as external parameters that modify the optical properties of the medium felt by the former. This is the case particularly when one of the fields is static or equivalently when its frequency is

zero, but often situations can be envisaged which involve static magnetic fields or other low frequency disturbances like acoustic waves. The fields of electro-optics, magneto-optics and acousto-optics are related to some very important applications and have great impact on device technology.

### 5. Electro-optics

This is related to changes of the refractive index of a material brought by a dc of low-frequency electric field. If this change is linear in the static field one has a linear electro-optic or Pockel's effect while when this change is quadratic in the static field, then one has the quadratic electro-optic effect or static Kerr effect. The former is related to a second order nonlinear polarization

$$P_i(\omega) = 2\chi_{ijk}^{(2)}(\omega, 0)E_j(\omega)E_{ok} \quad (11)$$

and can occur only for materials without inversion symmetry while the latter is related to a third order polarization

$$P_i(\omega) = 3\chi_{ijkl}^{(3)}(\omega, 0, 0)E_j(\omega)E_{ok}E_0^2 \quad (12)$$

which can occur in any material.

### 6. Magneto-optics

The oscillating magnetic field associated with a light beam is very weak with respect to the electric field to induce any sizeable effects but a static magnetic field  $H_0$  can be very intense and induce substantial changes in the optical properties as a consequence of the zeeman splitting that the degenerate magnetic levels undergo and the concomitant changes of the energy spacing and oscillator strengths.

The lowest order magneto-optic effect is related to the polarization

$$P(\omega) = 2\chi_M^{(2)}(\omega, 0)E(\omega)H_0 \quad (13)$$

and gives rise to the Faraday effect when the direction of  $H_0$  and that of the light beam propagation coincide. As for the Pockel's effect previously discussed, it is more convenient to first analyze the modification that the refractive index undergoes in the presence of the static magnetic field. One finds that here the refractive indices for right and left circular polarization become different and these two components experience different phase shifts after propagating a distance  $L$  inside the medium: the polarization state undergoes a rotation by an angle.

$$\theta_F = \omega L(n_- - n_+)/n_c. \quad (14)$$

## **7. Photorefractivity**

The photorefractive effect where the refractive index change induced by a light field when the crystal is subjected to intense laser radiation, defocusing and scattering of the light was observed, as a result of an inhomogeneous change in the refractive index. It was also found that these changes were maintained even after the light had been switched off, but could be erased by strong, uniform illumination. This index change is fundamentally different from the Kerr effect, which is responsible for the light-induced refractive index changes in conventional NLO materials. The Kerr effect, which is a fast response refractive index change, is quadratically dependent on the light-field amplitude. It is well-known in the area of optical soliton generation in fibers, in which it provides the necessary intensity-dependent phase shift for an optical pulse. Since it is a second order effect, it requires rather high intensities. Contrary to the photorefractive effect, the refractive index changes caused by the Kerr effect are entirely local, i.e. the change occurs at the spatial coordinate where the light hits the material.

The photorefractive effect, on the other hand, relies on carrier transport through inhomogeneous excitation by interfering laser beams. The diffused carriers affect the refractive index leading to a non-local change in the refractive index. This together with a high sensitivity enable refractive index changes at  $\sim$  mW laser radiation levels, constituting two of the major advantages of the photorefractive effect compared to the other NLO effects such as the Kerr effect. One of the drawbacks is the slow response due to slow diffusion of carriers. Hence materials which exhibit a local change in the refractive index will always, be faster. As a result of refractive index grating produced by the interfering beams, the photorefractive effect is sometimes also referred to as real-time holography since no development of any emulsion is necessary to store information by means of interference between a reference beam and an object beam. Holographic storage was indeed one of the first applications of the 'optical damage' considered. Erasable holographic memories were envisioned for three-dimensional mass storage devices. Phase-conjugation through degenerate four-wave mixing is used extensively because of its usefulness in image-deblurring applications, and investigations of material parameters often utilize two-beam coupling which is a special case of general photorefractive beam-coupling. A prerequisite for a material to be photorefractive is that it must not be a conductor, but an insulator or semi-insulator. Another requirement is transparency in the wavelength region of operation, which is very essential for applications such as holography and devices for optical signal processing. A third required property is the possibility of creating mobile carriers in the material. Photorefractivity research is multidisciplinary and involves crystal growth, solid-state physics, electronics, optics and electromagnetic wave coupling. The main difficulties encountered have been compatibility with other materials used for fabricating optical devices and difficulties to grow optical quality materials in large sizes with spectral sensitivities and response speeds suitable for available laser wavelengths. The typical photorefractive materials are  $\text{LiNbO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ ,  $\text{KbO}_3$ , BSO, KTN,  $\text{Ba}_2\text{SrNb}_5\text{O}_{15}$  and so on. Most of these materials are well known for their electro-optic and NLO properties. Semiconducting materials have gained much interest because of their high carrier mobilities and sensitivity in the infrared region and hence possess a commercial potential due to the advent of the infrared semiconductor lasers for optical communications. Some of the photorefractive semiconductors include InP, GaAs, GaP, CdTe and CdS. Semiconductor quantum well structures such as AlGaAs/GaAs can enhance the photorefractive effect over bulk materials via the

quantum confined stark effect. Because of the connection between the absorption and the refractive index through the Kramers-Kronig relations, a large electric-field induced absorption change such as the QCSE implies a high electro-optic (quadratic) response close to the bandgap. Another interest in the semiconductor photorefractive effect is utilizing of graded-gap quantum well structures, which provide a mechanism for carrier separation where the photogenerated carrier experiences an electric field corresponding to the spatial variation of the band energy levels. Illumination intensities required are much lower than those needed for the ordinary photorefractive effect. In addition, non-uniform illumination is not necessary since the charge transport is taken care of by the electric field instead of charge concentration gradients.

## **8. NLO materials**

NLO materials for integrated nonlinear optics pose stringent problems as regards their processability, adaptability and interfacing with other materials. These additional requirements are intrinsically related to the fabrication of nonlinear integrated devices, which besides efficiently performing the expected nonlinear operation, must be miniaturized, compact, reliable and with precisely reproducible characteristics in large-scale production and long term operation. On the basis of the three types of cohesive forces that bind the charges and polarization together, the NLO materials can be classified into the following cases: ionic crystals, which essentially consist of oxygen-polyhedra based solids, Covalent crystals essentially dealing with semiconductors and molecular crystals that with organic materials, disordered and amorphous solids, in particular glasses and polymers and composites and inhomogeneous artificial solids

The nonlinear frequency preserving effects are the ones that are most seriously considered in integrated optical devices. They can be either all optical or hybrid (parametric) effects. All optical nonlinearities essentially involve valence electron motion and are in general weaker than the hybrid ones where the ionic motion, vibrational, orientational or translational can set up very large nonlinearities; the situation however is reversed as regards the speed of establishing and erasing these nonlinearities, the electronic polarization being much faster than the ionic ones. The magnitude and speed of the nonlinearities are essential characteristics in any assessment of the material for NLO devices.

## **9. Organic crystals**

Conjugated DA substituted organic molecules exhibit measurable NLO and electro-optical effects. Such materials can be used to double or triple the frequency of laser light and are of considerable interest for the high-speed processing of data, which is essential for numerous modern technologies like optical computing and optical telecommunication systems. Some major applications are optical data storage, optical information processing, electro-optic switching and all-optic switching. Generally DA substituted compounds, where D and A are separated by an aromatic spacer group, represents the basis for all organic NLO compounds. The optical nonlinearity of organic molecules can be enhanced by adding strong electron donating and withdrawing entities as well as optimizing the distance

between D and A. This generates a highly polarizable charge transfer compound with an asymmetric electron distribution.

Optical storage and optical processing applications span interests from photochromics through spectral hole-burning materials, and to a particularly new class of materials called photorefractive polymers, where the light-induced generation of mobile charges, transport, and trapping are combined with second-order optical nonlinearity in a polymeric composite to form dynamic holograms. Charge separation produces internal electric fields, which locally alter the refractive index through the second-order optical nonlinearity. Polymer photorefractives are expected to be cheaper, easier to modify, and easier to fabricate into novel geometries than inorganic crystals. Both the polarizability anisotropy and the hyperpolarizability of the nonlinear chromophores are essential for the creation of strong holograms. The rationalization, computation, and prediction of NLO properties is thus a major field of interest in the research field of organic, physical, and theoretical chemistry as well as for the materials scientist. In spite of theoretical efforts, there is still no reliable way to predict first or even second order hyperpolarizabilities of organic DA compounds.

There is great demand for non centrosymmetric molecular crystals with large second order nonlinearities and with wide transparency range between the highest vibrational and lowest electronic transitions. The latter requirement is very restrictive regarding organic molecules and excludes the majority of them for further consideration in nonlinear optics. Among the remaining ones a large proportion is also excluded because they cannot form stable noncentrosymmetric crystals. This is mainly because asymmetric molecules most frequently carry a dipole moment in their ground electronic state and in order to reduce the dipole-dipole interaction, which is dominant over the van der Waals in the lattice, a head to tail antiparallel configuration will be favored when forming the crystal most frequently resulting in centrosymmetric crystalline structures and consequently vanishing  $\chi_E^{(2)}$  unless certain precautions are taken to prevent this from happening.

## **10. Disordered oriented media**

In guest-host polymer materials the nonlinear molecule is not attached to the polymer chain and thus can freely rotate close to glass transition temperature ( $T_g$ ). In side-chain (co) polymers, one end of the nonlinear molecule chemically reacts and is covalently attached or grafted on the polymer chain but the other end is free. In the case of cross-lined polymers, both ends of the nonlinear molecule chemically react and are covalently attached with the polymer chains. But in the main-chain systems the guest molecule is inserted in the chain.

Recently organic compounds with delocalized conjugated p-electrons have gained much attention because of their large NLO properties and quick response. Organometallic and coordination complexes materials exhibit novel NLO behavior. Second order NLO materials have the ability to double the frequency of incident light and have important commercial applications. Typical NLO molecules must have a dipole and be polarizable. In practice conjugated molecules with donor and acceptor groups on opposite ends of a conjugated chain are often used. Second order NLO materials must also have the correct alignment of molecules in the solid state. This is necessary to avoid having the individual molecular dipoles pairing up and effectively canceling each other out.

## 11. Semiconductors

Covalent semiconductors like Ge or GaAs possess the largest non-resonant cubic nonlinearities among all known crystals but these are unexploitable for several reasons, the most severe being the low absorption threshold in these compounds. On the other hand large and exploitable cubic optical nonlinearities can be produced by generating a finite concentration of electron hole pairs by resonant excitation above the bandgap. These large resonant nonlinearities have their origin in the band filling mechanism whereby the photoelectrons and holes quickly thermalize and fill all states in the bottom of the conduction and the top of the valence bands respectively up to levels that depend on the light intensity and pulse or recombination times, excluding those states that form on further occupation because of the Fermi principle. This blocking mechanism appears as a repulsion of the states on either side of the forbidden energy gap or equivalently as a blue shift of the absorption threshold: at very high intensities this mechanism leads to a saturation of the nonlinearity.

## 12. Composites semiconductor and metal nanocrystals in glasses

A way to enhance the cubic nonlinearities of materials with very delocalized electrons, like metals, semiconductors or conjugated polymers is to artificially confine the valence electrons in regions much shorter than their natural delocalization length in the bulk, which extends over many unit cells or even to infinity; its more conspicuous feature is the appearance of broad but discrete optical resonances whose position, oscillator strength, and dynamics depend on the extension of the artificial confinement and hence can be modified to meet certain requirements. The morphology related resonances result from two types of confinement: quantum and dielectric. The first one prevails in semiconductor nanocrystals while second one in metal nanocrystals. The dielectric confinement resides in the difference of the dielectric constants between the crystallites and their surrounding transparent medium. Because of this dielectric inhomogeneity the electric field  $E_{\omega l}$  that effectively polarizes the charges in these crystallites can be substantially different from the macroscopic Maxwell field  $E_{\omega}$  in the composite. Under certain simplifying conditions one can show that the relation between these two fields is

$$E_{\omega l} = \frac{3\epsilon_0}{\epsilon_m(\omega) + 2\epsilon_0} E_{\omega} \equiv f\delta(\omega)E_{\omega} \quad (15)$$

The quantum confinement occurs when the electron and hole envelopes are restricted within a region of extension  $L$  equal or smaller than the electron and hole Bohr radii,  $a_e$  and  $a_h$  respectively: the latter are defined in the bulk by the condition that the average value of the electron or hole kinetic energy roughly equals that of the potential. The confinement perturbs this balance, since these energies now vary as  $(a_c/L)^2$  and  $a_c/L$  respectively where  $a_c = a_c \cdot \epsilon$

$$E_c = \frac{1}{2}(e^2/a_c)(a_c/L)^2 \quad (16)$$

and as  $L$  decreases  $E_c$  increases and gradually suppresses the effect of the other interaction.

### **13. Thin film NLO materials**

The optical signal processing appears to be better in a number of ways. The signal carried by light is superior, in a certain sense, to that carried by an electric current. Electrons, which move in an electric circuit, are tiny charged particles, and as such they are attracted and repelled by other charges. Light also needs much less power to be transmitted through optical fiber lines, than electrical current does for transmission through coaxial lines. Light is a much 'finer' carrier that interacts very little with an appropriate transmission environment. Consequently, it is much less attenuated and distorted during transmission. This fact has been realized a while ago, and most of the communication nowadays relies on fiber optics. Optical data storage had an impressive take-off with CDs, however, there is still a noticeable gap in data processing, mostly due to the lack of reliable electro-optic devices. Many types of signals are genuinely optical, like in photo and video cameras, binoculars, photocopiers, spectrometers and overhead projectors. Optical processing seems only natural for these signals. Now the interest lies in thin-film NLO materials to be able to meet the huge demand in the years to come with the onset of IOCs as an alternative to silicon chips. The important premier NLO materials, like  $\text{KTiOPO}_4$  (KTP),  $\text{RbTiOPO}_4$  (RTP) and their derivatives have excellent chemical stability, ease of obtaining in crystalline form, wide working ranges of wavelength and temperature, high optical damage threshold and conversion efficiency ability to take the output of a number of widely used solid state lasers such as Nd:YAG and InGaAs.

### **14. Single crystals for EO, AO and nonlinear applications**

KDP( $\text{KH}_2\text{PO}_4$ ), DKDP( $\text{KD}_2\text{PO}_4$ ), ADP( $\text{NH}_4\text{H}_2\text{PO}_4$ ), lithium iodate BBO, LBO, CLBO, KTP, KTA,  $\text{KB}_5$ , tellurium dioxide, lead molybdate, silver thiogallate and silver selenogallate, zinc germanium phosphide, gallium selenide, BGO, BSO, LNB, LTA lithium tetraborate, barium nitrate. KDP, DKDP and ADP are widely used as the second, third and fourth harmonic generators for Nd:YAG and Nd:YLF lasers. Crystals are also widely used for electro-optical applications such as Q-switches for Nd:YAG, Nd:YLF, Ti:sapphire and alexandrite lasers and as well as for Pockel's cells. The most commonly used electro-optical crystal is DKDP with deuterium more than 98%. These crystals are grown by a solution growth method and can be grown into very large sizes. Therefore, these crystals are available as low-cost and large-size, finished nonlinear components. For frequency doubling (SHG) and tripling (THG) of Nd:YAG laser at 1064 nm, both type I and type II phase-matchings can be employed for KDP and DKDP. For frequency quadrupling (4HG, output at 266 nm) of Nd:YAG laser KDP crystal is normally used.

### **15. Current research in nonlinear optics**

#### *NLO polymers materials*

The widespread use of fiber optics in today's communications transmission systems is the first stage in a revolution of data processing and communications technologies based on optics rather than electronics. Current systems are expected to soon be drastically redesigned

to include faster optical and hybrid optical/electrical components. Basic research into the properties of the materials as well as applied research into the optimal use of these materials is greatly needed and is an important part of the activities for photon induced processes. NLO polymeric and liquid crystalline materials have been identified as strong candidates for emerging photonic data processing technologies. These materials consist in general of molecular fragments displaying NLO activity, or highly coloured chromophores, dissolved in or covalently attached to a polymeric host material. NLO polymers/liquid crystals possess vast potential for use in a variety of photonic systems, including high-speed optical modulators, ultra-fast optical switches, and high-density optical data storage media. These devices are essential for continued advancement in the effort to transform information storage and transmission from the electrical to the optical regime. The promise of NLO polymers lies in their fortuitous combination of exceptional optical qualities, low cost, and ease of fabrication into device structures. These technologically favorable characteristics have led to considerable research into the development of NLO polymers for commercial applications. A material suitable for widespread industrial use has yet to be synthesized, however. One of the most interesting and technologically promising phenomena applicable to some of these materials is the light-induced modulation of the index of refraction of the material through the photorefractive effect. Photorefractive materials combine photoconductivity and the electro-optic effect. Photorefractive nonlinear optics is by far the most efficient technique for causing beams of light to interact. Holograms can be written and erased in photorefractive media with low power lasers, and the intrinsic phase shift in the holographic grating can lead to energy exchange between the writing beams. With the growing use of fiber optics and optical communications technologies, photorefractive materials have become prime candidates for all-optical data processing applications. They are expected to be used for high density optical data storage, associative image processing techniques including dynamic holography and image amplification, spatial light modulation, programmable interconnections in integrated optics and simulations of neural networks and associative memories with parallel signal processing. Polymers and liquid crystals have emerged in recent years as exceptional candidates for photo-refraction, but much work in material development and characterization remains to be done.

## 16. Conclusion

The fundamental aspects of nonlinear optics and materials have been discussed in connection with their various applications to information storage technology.

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