Nonlinear Optical Materials

Nonlinear optics is the branch of science that deals with the interaction of light with matter under circumstances such that the linear superposition principle is violated. Examples of nonlinear optical interactions include harmonic generation, sum- and difference-frequency generation, the intensity dependence of the complex refractive index, light-by-light scattering, and stimulated light scattering. These processes lead to applications including all-optical switching, optical power limiting, image manipulation, and image processing.

Under many circumstances, the nonlinear optical response of a material system to an applied optical wave can be described by expressing the material polarization, $\tilde{P}(t)$, as a power series expansion in the electric field, $\tilde{E}(t)$, as

$$\tilde{P}(t) = \chi^{(1)}\tilde{E}(t) + \chi^{(2)}\tilde{E}^2(t) + \chi^{(3)}\tilde{E}^3(t) + \cdots \quad (1)$$

where $\chi^{(1)}$ is the linear susceptibility; $\chi^{(2)}$ is the second-order susceptibility, which describes processes such as second harmonic generation; and $\chi^{(3)}$ is the third-order susceptibility, which describes processes such as third-harmonic generation and the intensity-dependent refractive index. As written, Eqn. (1) applies to a material with instantaneous response. More generally, one can describe dispersive materials by allowing the linear and nonlinear susceptibilities to be frequency dependent. In addition, the nonlinear optical susceptibilities are in fact tensors, because they represent the relationship between the polarization, which is itself a vector, and the product of several electric field vectors. Such generalizations are described in standard reference works on nonlinear optics (Bloembergen 1964, Boyd 1992, Butcher and Cotter 1990, Hannah *et al.* 1979, Shen 1984, Sutherland 1996).

A primary consideration in selecting materials for applications of nonlinear optics is that the nonlinear susceptibility be adequately large. But other important criteria include the requirements that the material be highly transmitting at all wavelengths of interest, be highly resistant to laser damage, have fast temporal response, and be chemically stable.

1. Second-order Materials

1.1 Noncentrosymmetric Crystals

Insulating crystals form an important class of second-order nonlinear optical materials. It is well established that only crystals that lack a center of inversion symmetry can possess a nonvanishing second-order susceptibility. This requirement limits the choice of crystals to those of certain symmetry classes. An additional requirement on materials properties is set by the fact that second-order nonlinear optical processes can occur with good efficiency only if a standard phase matching condition is satisfied. This condition requires that the spatial variation of the nonlinear polarization be synchronous with that of the generated field, or mathematically that $\Delta k = k_3 - k_2 - k_1$ be much smaller than the inverse of the length, L, of the interaction region. Here k_3 is the wavevector of the highest frequency wave, and k_1 and k_2 are those of other waves. Because of the frequency dependence (dispersion) of the refractive indices, the phase matching condition has often been satisfied by using birefringent materials and by allowing the birefringence to compensate for dispersion. However, not all crystals with large second-order nonlinearities possess birefringence adequately large for this method to be used, and thus phase matching by means of birefringence imposes further restrictions on the choice of crystals for use in second-order nonlinear optics. The optical properties of some important crystals for use in second-order nonlinear optics are reviewed in Table 1. More extensive lists of second-order crystals and their properties can be found in standard reference works (Sutherland 1996), in manufacturers' specifications (e.g., Cleveland Crystals Inc., Cleveland, OH, provides data sheets, which may also be obtained at http://www.clevelandcrystals.com), and in public-domain databases (e.g., at http://www.sandia.gov/imrl/XWEB1128/xxtal.htm).

1.2 Periodically Poled Materials

Birefringence phase matching, described above, can suffer from certain limitations, including limited wavelength tuning range, smaller nonlinear coefficients, elevated phase-matching temperatures, awkward coupling angles, and the associated Poynting vector walk-off. An alternative approach, known as quasiphase matching, entails periodically inverting the sense of the nonlinear coefficient in order to compensate for the accumulated phase mismatch. The generated signal amplitude in the cases of true (i.e., birefringence) phase matching, quasiphase matching, and nonphase matching is depicted in Fig. 1 as a function of propagation distance within the material. It can be seen that without phase matching the amplitude of the generated wave cannot experience large growth, but that with quasiphase matching the generated wave experiences monotonic growth with an amplitude almost as large as that for true phase matching. The most common method for reversing the nonlinearity is electric field periodic poling (Myers and Bosenberg 1997), but ion and electron beams (Mizuuchi and Yamamoto 1993, Kurimura *et al.* 1996), diffusion bonding (Zheng *et al.* 1997, Gawith *et al.* 1999), and form birefringence (Van der Ziel 1975, Fiore *et al.* 1998) have also been investigated. Lithium niobate (Myers *et al.* 1995) has been used extensively in quasiphase matching. Potassium titanyl phosphate (Chen and Risk 1994), rubidium titanyl arsenate (Karlsson *et al.* 1996), lithium tantalate (Mizuuchi and Yamamoto 1996, Meyn and Fejer 1997), barium

Table 1
Properties of various second-order nonlinear optical materials.

Crystal (class)	Transmission range (μm)	Refractive index (at 1.06 μm)	Nonlinear coefficient (pm V^{-1})	Damage threshold (GW cm^{-2})
Silver gallium selenide, AgGaSe$_2$ ($\bar{4}2m$)	0.78–18	$n_o = 2.7010$ $n_e = 2.6792$	$d_{36} = 33$ (at 10.6 μm)	0.25 for 10 ns
β-Barium borate, BBO (3m)	0.21–2.1	$n_o = 1.6551$ $n_e = 1.5425$	$d_{22} = 2.3$ $d_{24} = d_{15} \leqslant 0.1$	4.6 for 1 ns, 15 for 0.1 ns
Lithium iodate, LiIO$_3$ (6)	0.31–5	$n_o = 1.8517$ $n_e = 1.7168$	$d_{31} = -7.11$ $d_{33} = -7.02$ $d_{14} = 0.31$	∼0.5
Lithium niobate, LiNbO$_3$ (3m)		$n_o = 2.234$ $n_e = 2.155$	$d_{31} = -5.95$ $d_{33} = -34.4$	
Potassium dihydrogen phosphate, KH$_2$PO$_4$ (KDP)	0.18–1.55	$n_o = 1.4944$ $n_e = 1.4604$	$d_{36} = 0.63$	
KTiOPO$_4$, KTP (mm2)	0.35–4.5	$n_x = 1.7367$ $n_y = 1.7395$ $n_z = 1.8305$	$d_{31} = 6.5$ $d_{32} = 5.0$ $d_{33} = 13.7$ $d_{24} = 6.6$ $d_{15} = 6.1$	

From a variety of sources. By convention, $d = \frac{1}{2}\chi^{(3)}$. The tensor nature of the nonlinear coefficients is expressed in contracted notation, in which the first index of d_{il} represents any of the three Cartesian indices and the second index, l, represents the product of two Cartesian indices according to the rule $l = 1$ implies xx, $= 2$ implies yy, $= 3$ implies zz, $= 4$ implies yz or zy, $= 5$ implies zx or xz, and $= 6$ implies xy or yx. To convert d_{il} to the Gaussian c.g.s. units of cm statvolt^{-1}, each entry should be divided by 4.189×10^{-4}.

titanate (Setzler *et al.* 1999), and potassium niobate (Meyn *et al.* 1999) have all been periodically poled successfully. In addition to high effective nonlinearities, low coercive fields, a wide transparency range, and low photorefractivity are also important in material selection.

1.3 Poled Organic Materials

Many asymmetric organic molecules have large values of the molecular hyperpolarizability, β. Electron delocalization along a conjugated backbone is shown in Fig. 2. In this example the nitrogen with the single bond donates an electron and either of the triple-bonded nitrogen atoms at the other end of the molecule accepts an electron. The second-order effects result from this electronic asymmetry. In bulk non-crystalline organic materials, however, the active species are oriented randomly, yielding no net effect over a length scale greater than molecular dimensions. To scale the large molecular nonlinear effect up to a useful level, some type of ordering is necessary. There are several methods in use to build up long ordered lengths. One is to use organic materials in crystalline form. Another method is to fabricate layered film structures through Langmuir–Blodgett and other techniques. Here the single-molecule nonlinear layer alternates with a layer of spacer molecules so that the nonlinear molecules are all oriented in the same direction. The most widespread technique involves incorporating the nonlinear species into a polymer either directly as a side chain, or in close proximity

(Service 1995) followed by poling. Three types of poling employed are photoassisted (Sekkat and Dumont 1992), all optical (Chalupczak *et al.* 1996), and thermal (Singer *et al.* 1986). In thermally assisted poling, the polymer is first heated above its glass transition temperature and then cooled while under a strong electric poling field. As the polymer cools the ordering is fixed. Research focuses on increasing the long-term stability of the ordering as well as on increasing nonlinearities.

2. Third-order Materials

Third-order materials play a crucial role in many applications of nonlinear optics. The third-order response leads to processes such as third harmonic generation and two-photon absorption, but more importantly leads to the intensity-dependent refractive index, which is the basis of most nonlinear optical switching devices. The intensity dependence of the refractive index is described by

$$n = n_0 + n_2 I \qquad (2)$$

where I is the laser intensity and n_2 is the coefficient of the intensity-dependent refractive index. This quantity can be related to the nonlinear susceptibility by means of (e.g., Boyd 1992, Eqn. (4.1.19))

$$n_2 = 12\pi^2 \chi^{(3)} / n_0^2 \qquad (3)$$

When the intensity is measured in units of W cm^{-2}
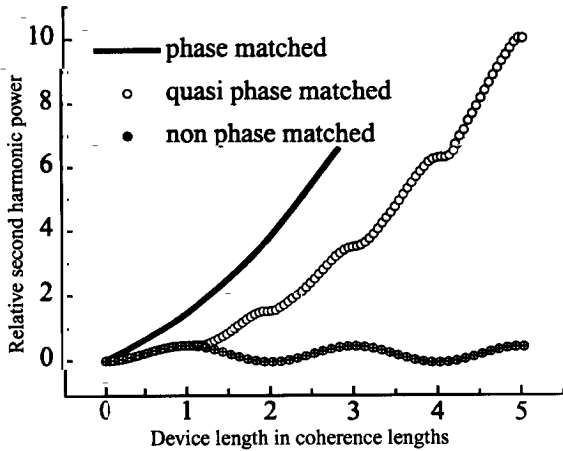
Figure 1
Growth of second-harmonic power in a nonlinear crystal as a function of crystal length in coherence lengths for conditions of perfect, i.e., birefringence phase matching, quasiphase matching, and nonphase matching.
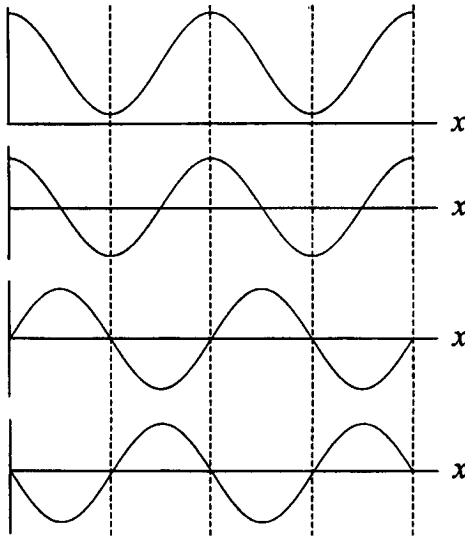
Figure 2
Origin of the photorefractive effect.

and $\chi^{(3)}$ in electrostatic units (esu), i.e., in $cm^2\,statvolt^{-2}$, the relationship between n_2 and $\chi^{(3)}$ becomes $n_2\,(cm^2\,W^{-1}) = 0.0395\chi^{(3)}(esu)/n_0^2$.

The third-order nonlinear optical properties of a variety of materials are listed in Table 2. Obviously, this list is by no means complete. The intention of Table 2 is to provide a survey of typical values of the third-order susceptibility for a variety of types of materials. More complete tabulations of nonlinear optical coefficients are given elsewhere (e.g., Sutherland 1996, Chase and Van Stryland 1995).

2.1 Insulating Solids

Materials such as insulating crystals and optical glasses typically possess nonlinear optical coefficients, $\chi^{(3)}$, of the order of 10^{-13}–10^{-14} esu. Electronic polarization is believed to make the largest contribution to the nonlinear response of these materials. This process has a very fast response time of the order of 10^{-15}–10^{-14} s. Quantum mechanical calculations show that the third-order susceptibilty resulting from electronic polarization will be of the order of (e.g., Boyd 1992, Eqn. (5.3.37))

$$\chi^{(3)} \cong \frac{N|\mu_{ba}|^4}{\hbar^3(\omega_0 - \omega)^3} \tag{4}$$

where N is the number density of atoms (or more generally the number density of optically active electrons if each atom possesses more than one outer-shell electron), μ_{ba} is a characteristic value of the dipole transition moment connecting the ground and an excited state, ω_0 is a characteristic resonance frequency of the atom, and ω is the frequency of the incident light wave. For the common situation in which ω is very much smaller than ω_0, this equation becomes simply

$$\chi^{(3)} \cong \frac{N|\mu_{ba}|^4}{\hbar^3\omega_0^3} \tag{5}$$

Several semiempirical models have been developed which make more precise predictions of the electronic contribution to nonlinear optical susceptibility (Miller 1964, Wynne 1969, Wang 1970, Boling *et al.* 1978, Hellwarth 1977, Boyd 1996, 1999). In many materials electrostriction makes an appreciable (perhaps 20%) contribution to the third-order susceptibility. Electrostriction has a response time of the order of 1 ns. The contribution of electrostriction to the third-order nonlinear polarization is described by (e.g., Boyd 1992, Eqn. (8.2.16))

$$\chi^{(3)} = \frac{1}{48\pi^2}C\gamma_e^2 \tag{6}$$

where γ_e is the electrostrictive coefficient defined by $\gamma_e = \rho(\partial\varepsilon/\partial\rho)$ and C is the compressibility defined by $C = (1/\rho)(\partial\rho/\partial p)$, where ε is the dielectric constant, ρ is the density, and p is the pressure.

2.2 Semiconductors

Semiconductors often possess a large third-order susceptibility, typically in the range 10^{-13}–10^{-10} esu. For a given material, the actual value of the susceptibility is usually strongly wavelength dependent, depending critically on the relative value of the photon

Table 2
Third-order nonlinear optical coefficients of various materials.

Material	n_0	$\chi^{(3)}$ (esu)	n_2 (cm^2 W^{-1})	Comments[a]
Crystals				
Al_2O_3	1.8	2.2×10^{-14}	2.9×10^{-16}	1
CdS	2.34	7.0×10^{-12}	5.1×10^{-14}	1, 1.06 μm
Diamond	2.42	1.8×10^{-13}	1.3×10^{-15}	1
GaAs	3.47	1.0×10^{-10}	3.3×10^{-13}	1, 1.06 μm
Ge	4.0	4.0×10^{-11}	9.9×10^{-14}	2, THG $|\chi^{(3)}|$
LiF	1.4	4.4×10^{-15}	9.0×10^{-17}	1
Si	3.4	2.0×10^{-10}	2.7×10^{-14}	2, THG $|\chi^{(3)}|$
TiO_2	2.48	1.5×10^{-12}	9.4×10^{-15}	1
ZnSe	2.7	4.4×10^{-12}	3.0×10^{-14}	1, 1.06 μm
Glasses				
Fused silica	1.47	1.8×10^{-14}	3.2×10^{-16}	1
As_2S_3 glass	2.4	2.9×10^{-11}	2.0×10^{-13}	3
BK-7	1.52	2.0×10^{-14}	3.4×10^{-16}	1
BSC	1.51	3.6×10^{-14}	6.4×10^{-16}	1
Pb Bi gallate	2.3	1.6×10^{-12}	1.3×10^{-14}	4
SF-55	1.73	1.5×10^{-13}	2.0×10^{-15}	1
SF-59	1.953	3.1×10^{-13}	3.3×10^{-15}	1
Nanoparticles				
CdSSe in glass	1.5	1.0×10^{-12}	1.8×10^{-14}	3, nonres.
CS 3-68 glass	1.5	1.3×10^{-8}	2.3×10^{-10}	3, res.
Gold in glass	1.5	1.5×10^{-8}	2.6×10^{-10}	3, res.
Polymers				
Polydiacetylenes				
PTS		6×10^{-10}	3×10^{-12}	5, nonres.
PTS		-4×10^{-8}	-2×10^{-10}	6, res.
9BCMU			1.9×10^{-10}	7, $|n_2|$, res.
4BCMU	1.56	-9.2×10^{-12}	-1.5×10^{-13}	8, nonres.
				$\beta = 0.01$ cm MW^{-1}
Liquids				
Acetone	1.36	1.1×10^{-13}	2.4×10^{-15}	9
Benzene	1.5	6.8×10^{-14}	1.2×10^{-15}	9
Carbon disulfide	1.63	2.2×10^{-12}	3.2×10^{-14}	9, $\tau = 2$ ps
CCl_4	1.45	8.0×10^{-14}	1.5×10^{-15}	9
Diiodmethane	1.69	1.1×10^{-12}	1.5×10^{-14}	9
Ethanol	1.36	3.6×10^{-14}	7.7×10^{-16}	9
Methanol	1.33	3.1×10^{-14}	6.9×10^{-16}	9
Nitrobenzene	1.56	4.1×10^{-12}	6.7×10^{-14}	9
Water	1.33	1.8×10^{-14}	4.1×10^{-16}	9
Other materials				
Air	1.0003	1.2×10^{-17}	5.0×10^{-19}	10
Ag		2.0×10^{-11}		2, THG $|\chi^{(3)}|$
Au		5.4×10^{-11}		2, THG $|\chi^{(3)}|$
Vacuum	1	2.4×10^{-33}	1.0×10^{-34}	11
Cold atoms	1.0	5.1	0.2	12, (EIT BEC)
Fluorescein dye in glass	1.5	$2 + 2i$	$0.035 (1 + i)$	13, $\tau = 0.1$ s

Here n_0 is the linear refractive index. The third-order susceptibility, $\chi^{(3)}$, is defined by Eqn. (1). This definition is consistent with that introduced by Bloembergen (1964). Some workers use an alternative definition that renders their values four times smaller. In compiling this table the literature values have been converted when necessary to the definition of Eqn. (1). β is the coefficient describing two-photon absorption.

energy of the incident light beam and the bandgap energy of the semiconductor. For photon energies smaller than the bandgap energy, there is no fundamental difference between a semiconductor and an insulating solid. In fact, scaling laws (Sheik-Bahae *et al.* 1990) that predict the dispersion of third-order susceptibility of semiconductors for below-gap conditions appear to be equally valid for insulting solids. A key conclusion of these scaling laws (Sheik-Bahae *et al.* 1990) is that $\chi^{(3)}$ changes sign as a the laser frequency is increased, being positive when the photon energy is less than approximately two-thirds of the bandgap energy and being negative for higher frequencies. For photon energies near the bandgap energy, the domi-

nant nonlinear optical mechanism is usually saturation of the exciton resonance of the semiconductor material. For photon energies greater than the bandgap energy, the nonlinear response occurs as the result of the excitation of electrons from the valence band to the conduction band, leading to a change in the optical properties as the result of processes such as screening of the Coulomb potential, reduction of the bandgap, and filling of the conduction band. Detailed descriptions of semiconductor nonlinearities can be found elsewhere (Butcher and Cotter 1990, Chap. 8, Peyghambarian and Koch 1990).

2.3 Photorefractive Materials

The photorefractive effect is the change in refractive index in a material owing to the optically induced redistribution of electrons and holes. The origin of the photorefractive effect is shown in Fig. 3. In the top curve two interfering beams form a spatially varying intensity pattern. In the next curve electrons have diffused away from the regions of highest intensity giving rise to a modulated charge distribution. The electric field is plotted in the following curve. The bottom curve shows the refractive index variation that is produced through the linear electrooptic effect by the electric field. A photorefractive material must be electrooptic, possess photocarrier trap sites, and be photoconductive. The photorefractive effect was first observed as reversible crystal damage and lowers the efficiencies of the processes described in Sect. 1. Under a wide range of conditions the change in refractive index is independent of the intensity of the light that induces the change. Several classes of materials exhibit photorefractive properties. Among the insulating materials, $BaTiO_3$, with a nonlinear coefficient of $n^3 r^{eff} = 11\,300\,pm\,V^{-1}$, is the most photorefractive material. InP, GaAs, and CdTe are three important photorefractive semiconductors. Materials of these two classes are discussed in Günter and Huignard (1988). Multiple quantum wells have refractive index changes as large as 0.01, saturation intensities of the order of $10\,\mu W\,cm^{-2}$, and microsecond response times. The photorefractive effect in polymers has also been reported (Durcharme *et al.* 1991). In polymer research, efficient carrier transport agents and photo-sensitizers can be developed separately and then synthesized to form a polymer with superior characteristics. Unlike crystals, polymers can incorporate a large percentage of dopants; however, the electrooptic chromophores must be aligned. More information on many aspects of photorefractive materials can be found in Yeh (1993) and Nolte (1995).

2.4 Organic Materials

Some of the largest nonlinearites reported have been measured in organic materials. Polydiacetylene and its derivatives can have nonresonant nonlinear optical susceptibilities, $\chi^{(3)}$, of the order of 10^{-10} esu with femtosecond response times. Delocalized π-electrons, which are free to travel along the conjugated structure or backbone of molecules and polymers, are the key factor to high nonlinearities in organic materials. Two derivatives of polydiacetylene are shown in Fig. 4. Only the group labeled R is used in the polymer 4-BCMU. In BPOD both groups shown in Fig. 4 are used (Kim *et al.* 1994). Specific information can be found in Zyss (1994) and Prasad and Williams (1991). Organic molecules with coordinated metal ions such as phthlalocyanine and porphyrin (Philip *et al.* 1999) also have promising nonlinearities. The structure of phthalocyanine is shown in the lower part of Fig. 4. The effect of central metal ion on nonlinearity has been investigated (Shirk *et al.* 1992). Another interesting area of research in derivatives of these molecules involves the addition of ring structures to the central molecule (Yamashita *et al.* 1998).

2.5 Liquids

The nonlinear optical response of liquids typically results from a combination of three mechanisms: (i) molecular orientation, with a timescale of the order of 1 ps and a nonlinear optical susceptibility, $\chi^{(3)}$, of the order of 10^{-12} esu, (ii) electrostriction, with a timescale of the order of 1 ns and $\chi^{(3)}$ of the order of 10^{-13} esu, and (iii) electronic polarization, with a timescale of the order of 1 fs and $\chi^{(3)}$ of the order of 10^{-14} esu. The largest contribution, molecular orientation, can occur only for liquids containing asymmetric molecules. Consequently the nonlinear susceptibility of liquids containing asymmetric molecules (such as carbon disulfide) tends to be much larger than that of liquids containing symmetric molecules (such as carbon tetrachloride). The mathematical expression for the contribution to the third-order susceptibility resulting from molecular orientation is (e.g., Boyd 1992, Eqn. (4.4.24))

$$\chi^{(3)} = \frac{4N(\alpha_3 - \alpha_1)^2}{75kT} \tag{7}$$

where N is the number density of molecules and $(\alpha_3 - \alpha_1)$ is the difference in polarizabilities along the principal dielectric axes of the molecule. The nonlinear optical properties of some typical liquids are given in Table 2. The nonlinear optical properties of liquids are discussed in detail in Hellwarth (1977).

2.6 Composite Materials

Very large nonlinear optical effects are often observed in composite materials. For example, by embedding semiconductor or metallic nanoparticles in a glass host
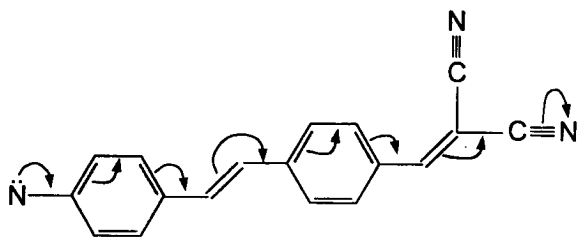
Figure 3
Donor–acceptor organic molecule with conjugated bonds.

(a)

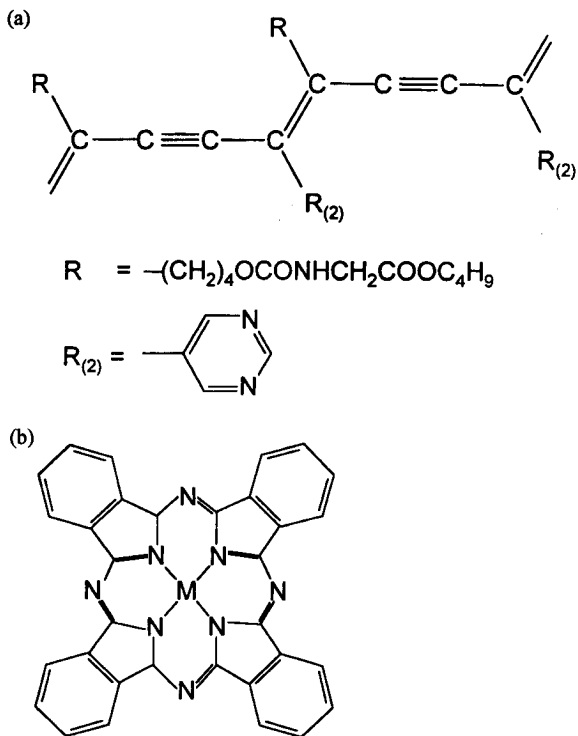$$R = -(CH_2)_4OCONHCH_2COOC_4H_9$$

$R_{(2)} =$

(b)

Figure 4
Promising organic material structures for third-order nonlinear optics. (a) Structure of polydiacetylene. In 4-BCMU only the top R structure is used. Both R and R2 are used in the synthesis of BPOD. (b) Phthalocyanines and their derivatives. Here M is any of a number of metals or organometallic groups.

with a volume concentration as small as 10^{-6}, a nonlinear susceptibility as large as 10^{-8} esu, some six orders of magnitude larger than the glass host, can be obtained. There are several physical mechanisms that can lead to an increase in the nonlinear susceptibility of a composite material. One approach is to embed a glass host with some other material (such as a semiconductor) that possesses a large resonant non-linearity. In such a case the host serves primarily as a
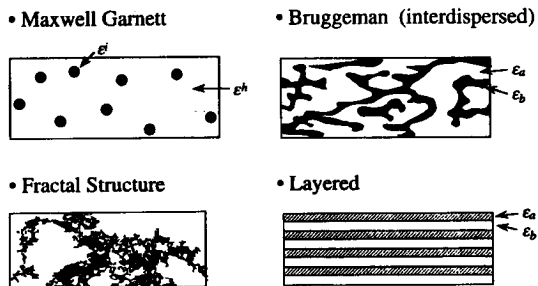

Figure 5
Composite material structures of interest in the development of nonlinear optical materials.

convenient mechanical support for the highly non-linear (but absorbing) nonlinear constituent. Another approach is to place metal nanoparticles within a glass host. Such a system displays a resonance known as the surface plasmon resonance. At the resonance frequency, the electric field strength within the metallic particles can be enhanced over the incident field strength by many orders of magnitude, leading to an enhanced nonlinear optical response (Hache *et al.* 1988). Another approach (Sipe and Boyd 1992, Boyd and Sipe 1994, Fischer *et al.* 1995) is to combine two materials in such a manner that local field effects lead to a redistribution of electric field strength between the two constituents. Several geometries for doing so are shown in Fig. 5. If the electric field becomes concentrated in the more nonlinear constituent of the composite, the nonlinear susceptibility of the composite can exceed those of its constituent materials. The advantage of this approach is that it can lead to an enhancement even for nonresonant (lossless) materials. A three-fold increase in $\chi^{(3)}$ has been observed based on this approach (Nelson and Boyd 1999).

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