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Nonlinear Optical Effects in Polar Dielectric Materials

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Abstract. The electro-optical and nonlinear optical properties of organic materials are reviewed. Molecular crystals, *Langmuir-Blodgett* films and poled polymers are shown to have interesting properties for applications as high-speed electro-optic modulators, optical frequency converters or all optical signal processors.

Introduction

Recent developments in the field of nonlinear optics hold promise for important applications in optical information processing, telecommunication and integrated optics. Electro-optic, nonlinear optical and photorefractive materials are active media which can be used in a variety of devices in which light waves have to be manipulated by electrical and optical fields.

With the improvement of quality and output power of diode lasers, it is expected that instruments and systems employing lasers will be used more and more. Light, especially a laser beam, has a number of beneficial characteristics, thanks to its good coherence, high density, parallel processing ability, high speed responsivity and diverse wavelength and frequency. All of these characteristics are essential for realizing high-speed, large-capacity information transmission and processing, high-density data recording and storage. In order to fully utilize the various optical functions of a laser beam, the second- or third-order nonlinear optical response of a material for an electrical field at optical or radio frequency is employed in one form or another. In particular, the development of electrically and optically controlled devices such as frequency converters, electro-optical modulators or photorefractive nonlinear devices employing the second-order nonlinear optical response, including the first-order electro-optic effect, is actively taking place.

Electro-optic and Photorefractive Effects

Electro-optic devices provide many basic functions for modulating and deflecting a laser beam. Electro-optic materials which in addition to the electric field induced changes of indices of refraction also show photoconductivity have been shown to be efficient nonlinear optical materials. It has been demonstrated, that optically released charge carriers from impurity ions can produce space-charge fields which lead to refractive index changes by the electro-optic effect. Since large photoinduced changes of refractive indices can be induced at low light intensities (mW level) nonlinear optical processing of arrays of pixels (images) can be achieved. Several applications of dynamic image processing using nonlinear optical and photorefractive materials have thus been proposed and investigated in recent years. They include: optical frequency conversion, electro-optic modulation and deflection, dynamic holography, real-time interferometry, optical storage, optical phase conjugation, optical image amplification, spatial light modulation, optically induced beam deflection and optical interconnection and several types of optical information processors *etc.* Most of the features of these applications critically depend on the materials used.

It has been known for many years that certain classes of organic materials exhibit extremely large nonlinear optical and electro-optical effects. The electronic nonlinearities in the most efficient organic materials are essentially based on molecular units containing highly delocalized π -electrons and additional electron donor and electron acceptor groups on opposite sides of the molecules. The most highly active molecules thus tend to be highly

polarized. The most polar molecules have a tendency to crystallize in a centrosymmetric structure which does not show a linear electro-optic effect. The choice of special molecules and the crystal growth methods used are of main importance for obtaining electro-optically active single crystals of good quality and large size. A main advantage of the organic materials is the possibility of altering the molecular structure for optimizing the electro-optic or nonlinear optical properties. For the future development in the field of nonlinear optical organic materials a multidisciplinary effort combining organic chemistry, crystal growth, materials science, physics and electrical engineering is essential. This review presents the results of the preparation, characterization and application of organic electro-optic materials in this emerging combination of fields including chemistry and physics.

Until recently, it was an open question whether the most active electro-optical molecular crystals can be made photoconductive. This combination of properties is the main requirement for the appearance of the photorefractive effect. It has been shown in 1990 that by doping 2-(cyclooctylamino)-5-nitropyridine (COANP) with 7,7,8,8-tetracyanoquinodimethane (TCNQ) also in organic materials one can observe photorefractive effects based on photoinduced space charge fields. If it would be possible in the future to optimize electro-optic properties and photoconductivity, the organic materials could prove useful also for applications in parallel optical signal processing or optical phase conjugation.

Nonlinear Optical Effects in Organic Material

There are known many interesting molecules that display strong nonlinear optical effects when deposited on substrates as *Langmuir-Blodgett* films, polymers or thin film crystals [1–8]. For applications there are two important requirements to be fulfilled. First, all wavelengths involved in the nonlinear optical effects should be away from the electronic resonances, that is below the absorption edge of the molecules. Secondly, for any kind of application non-centrosymmetric films or crystals have to be fabricated. *Table 1* shows examples of molecules with strong optical nonlinearities. The nonlinear optical coefficients d_{ijk} are defined by

$$P_i^{2\omega} = \epsilon_0 d_{ijk} E_j^\omega E_k^\omega$$

where summation over common indices is assumed. $P_i^{2\omega}$ is the induced macroscopic

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Table 1. Nonlinear Optical (d), Electro-optic (r), and Optical Properties of Inorganic and Organic Materials (r^T , r^s , and r^e are the electro-optic coefficients at constant stress, constant strain and at optical frequencies (electronic contribution, calculated from nonlinear optical susceptibilities)). Data at 632.8 nm (for electro-optics) and 1064 nm (nonlinear optics) except where noted (ϵ : dielectric constant).

Material	Symmetry	Refractive Index	r^T [pm/V]	r^s [pm/V]	r^e [pm/V]	d [pm/V]	ϵ	$n^2 = \epsilon_{\text{optical}}$
inorganic								
BaTiO ₃	4 mm	$n_3 = 2.480^a$	$r_{33} = 94 \pm 3^1$ $r_{13} = 19.5 \pm 0.5^1$ $r_{42} = 1700$	28 8 820	+0.85 +2.3 +2.3	$d_{33} = -6.7$ $d_{31} = -18$ $d_{24} = -18$	$\epsilon_{11} = 4300$ $\epsilon_{33} = 168$	6.2
KNbO ₃	mm2	$n_1 = 2.279$ $n_2 = 2.329$ $n_3 = 2.167$	$r_{33} = 64$ $r_{13} = 28$ $r_{42} = 380$	25 10 -	+5.0 +2.7 2.7	$d_{33} = -27.4$ $d_{31} = -18.3$ $d_{24} = -17.1$	$\epsilon_{11} = 160$ $\epsilon_{22} = 1000$ $\epsilon_{33} = 55$	5.2 5.4 4.7
LiNbO ₃	3 m	$n_1 = 2.272$ $n_3 = 2.187$	$r_{33} = 30.8$ $r_{13} = 9.9$	30.8 8.6	+5.8 +0.85	$d_{33} = -36$ $d_{31} = -5.3$	$\epsilon_{33} = 29$	5.2 4.8
KD ₂ PO ₄	42 m	$n_1 = 1.51$ $n_3 = 1.47$	$r_{63} = 26.4$ $r_{41} = 8.8$	24 -	0.39 0.39	$d_{36} = 0.53$ $d_{14} = 0.53$	50	2.3 2.2
GaAs	42 m	$n = 3.60$	$r_{41} = -1.5$	-1.5		$d_{14} = +140$	$\epsilon_{11} = 13.2$	13
organic								
MNA	m	$n_1 = 2.0$	$r_{11} = 67 \pm 25$	-	20 ± 14	$d_{11} = 250 \pm 50$	3.5	4
MMONS	mm2	$n_1 = 1.569$ $n_2 = 1.693$ $n_3 = 2.129$	$r_{33} = +19.3 \pm 4$ $r_{33} = 39.9 \pm 8$	-	19.3 ± 3.9 35.9 ± 7	$d_{33} = 184 \pm 37$ $d_{32} = 41 \pm 8$ $d_{24} = 55 \pm 28$	- 0	2.5 2.9 4.9
m-NA	mm2	$n_1 = 1.805$ $n_2 = 1.715$ $n_2 = 1.675$	$r_{33} = 16.7 \pm 0.2$ $r_{23} = 0.1 \pm 0.6$ $r_{13} = 7.4 \pm 0.7$	-	-	$d_{22} = 21$ $d_{32} = 1.6$ $d_{31} = 20$	$\epsilon_{11} = 3.2$ $\epsilon_{22} = 3.3$ $\epsilon_{33} = 3.2$	3.3 2.9 2.8
POM	22	$n_1 = 1.712$ $n_2 = 1.919$ $n_3 = 1.638$	$r_{41} = 3.6 \pm 0.6$ $r_{52} = 5.1 \pm 0.4$ $r_{63} = 2.6 \pm 0.3$	-	4.0 5.1 3.7	$d_{14} = 10$ $d_{25} = 10$ $d_{36} = 10$	$\epsilon_{11} = 3.77$ $\epsilon_{22} = 5.41$ $\epsilon_{33} = 3.77$	2.9 3.7 2.7
COANP	mm2	$n_1 = 1.672$ $n_2 = 1.781$ $n_3 = 1.647$	$r_{33} = 14.8 \pm 1.6$ $r_{23} = 12.9 \pm 1.5$	-	9.3 ± 1.5 15.4 ± 3.2	$d_{33} = 19.3 \pm 3$ $d_{32} = 43 \pm 9$ $d_{24} = 40 \pm 6$	$\epsilon_{11} = 2.8$ $\epsilon_{22} = 2.7$ $\epsilon_{33} = 2.6$	2.65 3.87 2.54
PNP	2	$n_1 = 1.990$ $n_2 = 1.788$ $n_3 = 1.467$	$r_{22} = 13.1 \pm 2$ $r_{23} = 13.1 \pm 2$	-	8.0 ± 1.4 13.0 ± 3.2	$d_{22} = 70 \pm 8$ $d_{23} = 21.6 \pm 4$ $d_{16} = 53.4 \pm 6$		4.0 3.3 2.2

^{a)} At $\lambda = 514.5$ nm.

polarization at frequency 2ω (polarized along the i direction). $E_{j,k}^\omega$ are the incident electric fields at ω (polarized along j, k), and ϵ_0 is the vacuum permittivity. For the ideal case of slightly focused monochromatic Gaussian beams, the second-harmonic intensity generated by the harmonic polarization $P^{2\omega}$ neglecting pump depletion, is given by

$$I^{2\omega} = \frac{2\omega^2}{\epsilon_0 c^3} \cdot \frac{d_{\text{eff}}^2}{n_\omega^2 n_{2\omega}} \cdot L^2 (I^\omega)^2 \text{sinc}^2\left(\frac{\Delta k L}{2}\right)$$

where $\text{sinc}(x) = (\sin x)/x$, L is the sample thickness, d_{eff} is the effective nonlinear optical susceptibility, c is the vacuum velocity of light and $\Delta k = k_1^{2\omega} - k_2^{2\omega} - k_3^{2\omega}$ is the phase mismatch between the funda-

mental and second-harmonic waves with wave-vectors k_1, k_2 , and k_3 , respectively.

The main materials constants describing the efficiency of optical frequency doubling is the materials parameter $d^2/n_\omega^2 n_{2\omega}$. Table 1 shows some measured values of the nonlinear optical susceptibilities d for a series of organic crystals in comparison to few inorganic materials. Table 2 shows similar data for some nonlinear optical polymers. These data indicates that improved efficiencies in nonlinear optical frequency conversion can be obtained by using organic materials. Some other materials parameters such as phase-matching conditions, optical damage threshold, residual absorption, chemical and optical stability also represent impor-

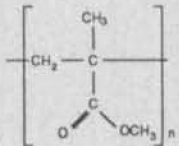
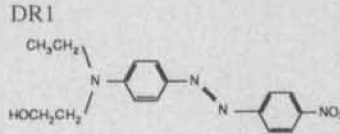
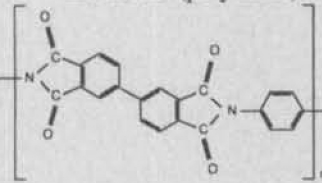
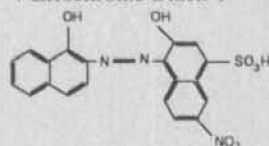
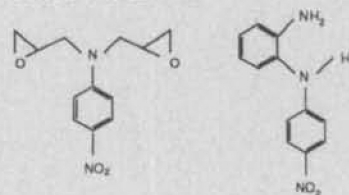
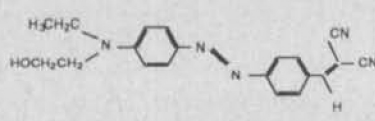
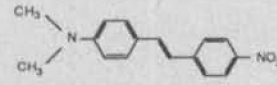
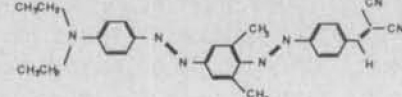
tant criteria for choosing a suitable material for nonlinear optical applications (see e.g. Chemla and Zyss).

The electro-optical coefficients r listed in Tables 1 and 2 describe the field-induced changes of the optical indicatrix (inverse of dielectric tensor at optical frequencies):

$$\Delta\left(\frac{1}{n^2}\right)_{ij} = r_{ijk} E_k$$

Three values have been given in Table 1. They apply for electric fields at different frequency. r^T is the low frequency (free) electro-optical coefficient measured below acoustic and optical lattice vibrational frequencies, r^s the clamped effect between acoustic and optical lattice reso-

Table 2. *Electro-Optic and Nonlinear Optical Properties of Selected Polymer Systems.* E_p : poling field, d : nonlinear optical susceptibility, λ : wavelength, T_g : glass transition temperature, r : electro-optic coefficient.

Typ ^{a)}	Matrix and Nonlinear optical moiety	E_p [V/ μm]	d [pm/V] (λ [nm])	r [pm/V] (λ [nm])	T_g [°C]	Reference
GH	PMMA 	37	$d_{33} = 2.5$	$r_{33} = 2.5$	—	[1]
GH	DR1 	—	$d_{33} = 84$ (1356)	—	—	[2]
GH	Pyralin 2611D (polyimide) 	50	—	—	≈ 320	[3]
	+ Eriochrome Black T 					
CL	NNDN + NAN 	—	$d_{31} = 14$ (1064)	$r_{33} = 6.5$ (530.9)	≈ 110	[4]
SC	PMMA + DCV 	—	$d_{33} = 21$ (1580)	$r_{33} = 18$ (799)	127	[5]
SC	^{b)} + DANS 	170	—	$r_{33} = 34$ (1300)	≈ 140	[6]
SC	^{b)} + DANS based	≈ 200	—	$r_{33} = 38$ (1300) $r_{33} = 98$ (633)		[7]
SC	PMMA + 3RDCVXY 	≈ 200	$d_{33} = 240$ (1064)	$r_{33} = 40$ (633)	< 140	[8]

^{a)} GH: guest host system, CL: croll sinked polymer, SC: side-chain polymer.
^{b)} Backbone polymer not known.

MNA	2-methyl-4-nitroaniline
MMONS	3-methyl-4-methoxy-4'-nitrostilbene
m-NA	p-nitroaniline
POM	3-methyl-4-nitropyridine 1-oxide
COANP	2-(cyclooctylamino)-5-nitropyridine
PNP	2-(N-prolinol)-5-nitropyridine
PMMA	poly(methyl methacrylate)
DRI	4-[N-ethyl-N-(2 hydroxyethyl)amino]-4'-nitroazobenzene (Disperse Red 1)
TCV	4-(tricyanovinyl)-4'-(diethylamino)azobenzene
NNDN	N,N-diglycidyl-4 nitroaniline
NAN	N-(2-aminophenyl)-4-nitroaniline
DCV	4-(dicyanovinyl)-4'-(dimethylamino)azobenzene
DANS	4-(dimethylamino)-4'-nitrostilbene
3RDCVXY	4-(dicyanovinyl)-4'-(diethylamino)diazobenzene

nances and r^e the effect at optical frequencies (electronic contributions). For high speed electro-optical light modulators and deflectors r^e should be as high as possible. Few measured data for r^e are available at present. Since lattice contributions are expected to be small in organic materials one usually approximates r^e with the purely electronic contribution r^e .

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NLO-Polymers and Their Applications in Devices

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Hyperpolarizable groups attached to polymers have been used as optically nonlinear materials for thin film guided wave, passive as well as active (electro-optic) devices. Multilayers comprising polymeric core and cladding layers thus forming slab waveguides on a substrate, have been prepared. Close to the glass transition temperature of the polymer (e.g. 140°), strong electric fields (100 V/μm) induced the electro-optic effect. Via UV bleaching through selected masks, channel waveguides have been realised by locally decreasing the refractive indices. Finally,

the metal top electrode was patterned. Passive (unpoled) as well as active guided wave structures such as: straight and bent channels, optical power splitters, phase modulators, Mach-Zehnder interferom-

eters and switches, have been made [1][2]. Switching voltages are ca. 10 V; the extinction ratio's are around 20 dB. The measured intensity output of an optical power splitter is shown in the Figure. Also thermo-optically switchable elements have been made; here, heating the waveguide changes the refractive index; electrical switching powers are of the order of 10's of mW's.

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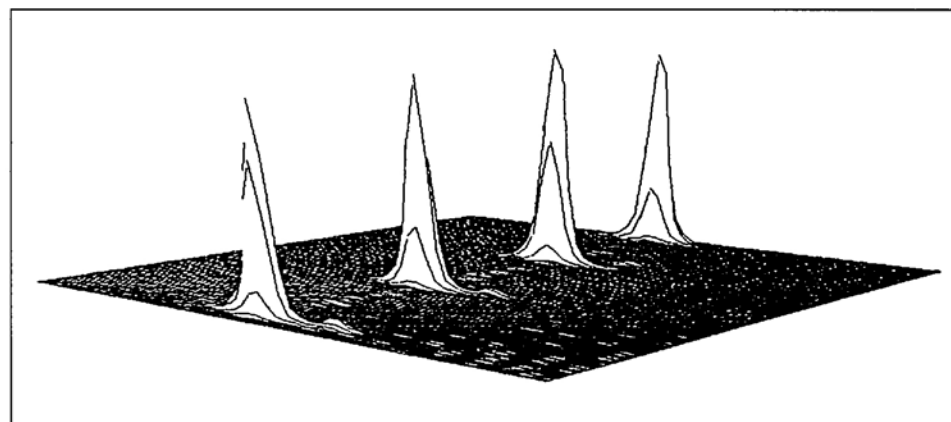


Figure. Output intensity profile of a 1*4 passive optical power splitter

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