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NONLINEAR OPTICAL PROPERTIES OF MONOLAYER FILMS DEPOSITED ON IR TRANSPARENT SUBSTRATES

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1. Introduction to nonlinear optics

- 2. Principal effects of nonlinear optics
- **3. Experimental set-up for realization of nonlinear opics**
- 4. Nonlinear optics of nanomaterials

Introduction to nonlinear optics

Polarization induced by a laser field



Second harmonic generation

$$P^{NL} = 2\varepsilon_0 dE^2$$

First demonstration of second-harmonic generation P.A. Franken (1961)



Figure 12.1. Arrangement used in the first experimental demonstration of second-harmonic generation [1]. A ruby-laser beam at $\lambda = 0.694 \,\mu$ m is focused on a quartz crystal, causing the generation of a (weak) beam at $\frac{1}{2}\lambda = 0.347 \,\mu$ m. The two beams are then separated by a prism and detected on a photographic plate.

The second-harmonic beam was very weak because the process was not phase-matched.

First demonstration of second-harmonic generation

The actual published results...



FIG. 1. A direct reproduction of the first plate in which there was an indication of second harmonic. The wavelength scale is in units of 100 A. The arrow at 3472 A indicates the small but dense image produced by the second harmonic. The image of the primary beam at 6943 A is very large due to halation.

Introduction to nonlinear optics

Generate field = solution of a wave equation

$$\nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{1}{\varepsilon c^2} \frac{\partial^2 P^{NL}}{\partial t^2}$$

Fundamental

$$E_{\omega}(z,t) = \frac{1}{2}E_1(z,t)e^{i\omega t - ik_{\omega}z} + cc \qquad k_{\omega} = \frac{n_{\omega}\omega}{c}$$

Harmonic generation

2nd harmonic

$$P_{2\omega}^{NL}(z,t) = \frac{1}{2} P_2(z,t) e^{2i\omega t - 2ik_{\omega}z} + cc$$

Different phase velocity
$$E_{2\omega}(z,t) = \frac{1}{2} E_2(z,t) e^{2i\omega t - ik_{2\omega}z} + cc$$

$$\propto e^{2ik_{2\omega}\alpha t - 2ik_{\omega}z}$$

$$i = \frac{2i\alpha t - ik_{2\omega}z}{2}$$

$$j = \frac{2i\alpha t - ik_{2\omega}z}{2}$$

The lengths of the problem



Phase-matching second-harmonic generation

 $n(2\omega) = n(\omega)$



Using birefringence

$$n_o(2\omega) = n_e(\omega)$$





Dependence of SHG intensity on length

Large Δk



Small Δk



The SHG intensity is sharply maximized if $\Delta k = 0$.

Wave vectors







References

Fundamentals of Photonics

Ch. 18 and 19

Nonlinear Optics

🗆 R. W. Boyd

Photonics: Optical Electronics in Modern Communications

- A. Yariv and P. Yeh
- Ch. 8, Ch. 9 and Ch. 14







Atomic origin of optical nonlinearity



Nonlinear polarization

Linear medium: low field intensity

$$D = \varepsilon_0 E + P \qquad P = \varepsilon_0 \chi \cdot E \qquad \qquad D = \varepsilon \cdot E = \varepsilon_r \varepsilon_0 E \qquad \varepsilon_r = 1 + \chi$$

Linear polarization

Nonlinear medium: high field intensity

$$D = \varepsilon_0 E + P \qquad P = \varepsilon_0 \chi \cdot E + \chi^{(2)} \cdot E^2 + \chi^{(3)} \cdot E^3 + \dots = P_L + P_{NL}$$

Nonlinear polarization

$$P_i = \varepsilon_0 \chi_{ij} \cdot E_j + 2D_{ijk} \cdot E_j E_k + 4\chi_{ijkl} E_j E_k E_l + \dots = P_L + P_{NL}$$

Linear 2 susceptibility r tensor su

2nd order nonlinear susceptibility tensor

3rd order nonlinear susceptibility tensor i, j, k = x, y, z

Summation over repeated indices

Nonlinear optical effects

- 2nd order optical nonlinear effects
 - Pockels/electro-optic effect
 - Second harmonic generation (SHG)
 - Sum/difference frequency generation (SFG/DFG)
 - Optical parametric amplification/oscillation (OPA/OPO)
- 3rd order optical nonlinear effects
 - Optical Kerr effect/quadratic Pockels effect
 - Third harmonic generation (THG)
 - Four wave mixing (FWM)
 - Two photon absorption (TPA)
 - Stimulated Raman/Brillion scattering (SRS/SBS)

General methodology for nonlinear optics

- Write the expression of electric field in medium
 - e.g. in an optical waveguide

 $\overline{E} = \operatorname{Re}[E_0 \cdot U(x, y) \cdot \exp(ik \cdot z - i\omega \cdot t)] = E_0 \cdot U(x, y) \cdot \exp(ik \cdot z - i\omega \cdot t) + c.c.$

- Calculate the linear and nonlinear polarization $P = \varepsilon_0 \chi \cdot E + \chi^{(2)} \cdot E^2 + \chi^{(3)} \cdot E^3 + ... = P_L + P_{NL}$
- Substitute in to the electromagnetic wave equation

$$\nabla^{2}\overline{E} = \mu_{0}\frac{\partial^{2}}{\partial t^{2}}(\varepsilon_{0}\overline{E} + \overline{P}) = \mu_{0}\varepsilon_{0}\frac{\partial^{2}\overline{E}}{\partial t^{2}} + \mu_{0}\frac{\partial^{2}}{\partial t^{2}}P_{NL}$$

Focus on the terms Source term with relevant frequencies

Pockels effect / Electro-optic (EO) effect

- 2nd order optical nonlinearity
- Externally applied electric field modifies the optical properties of materials
 - □ Refractive index, bifringence, etc.



Total electric field: $E = E_{light} + E_{ex} = \text{Re}[E_0 \cdot \exp(i\omega \cdot t)] + E_{ex}$

 $P_{NL} = \chi^{(2)} \cdot E^2 = \chi^{(2)} \{ \operatorname{Re}[E_0^2 \cdot \exp(i2\omega \cdot t)] + 2E_{ex} \operatorname{Re}[E_0 \cdot \exp(i\omega \cdot t)] + E_{ex}^2 + 2E_0 E_0^* \}$

$$\sim \chi^{(2)} \{ 2E_{ex} \cdot \text{Re}[E_0 \exp(i\omega \cdot t)] + E_{ex}^2 + 2E_0 E_0^* \} \sim 2\chi^{(2)} E_{ex} E_{light} \quad (\mathsf{E}_0 << \mathsf{E}_{ex}) \}$$

Polarization oscillating Static polarization at the optical frequency

Dielectric constant change due to 2nd order nonlinearity

$$\varepsilon_r = 1 + \chi + 2\chi^{(2)}E_x$$

Second harmonic generation (SHG)

- 2nd order optical nonlinearity
- Use light with wavelength λ = λ₀ to generate light with λ = λ₀/2
 □ Frequency doubling ω = 2ω₀

Total electric field: $E = E_{light} = \text{Re}[E_0 \cdot \exp(i\omega_0 \cdot t)]$



 $D = \sum_{ijk} D_{ijk} U_{2i} U_{1j} U_{1k}$

$$\chi^{(2)} \cdot E^2 \sim \chi^{(2)} \cdot \underline{\operatorname{Re}[E_0^2 \exp(i2\omega_0 \cdot t)]} \qquad \nabla^2 \overline{E} = \mu_0 \varepsilon_0 \frac{\partial^2 \overline{E}}{\partial t^2} + \mu_0 \frac{\partial^2}{\partial t^2} P_{NL}$$

diating dipole with a frequency $\omega = 2\omega_0$

Rigorous solution:

 $P_{NL} =$

Ra

$$\overline{E_1} = E_{10} \cdot U_1(x, y) \cdot \exp(ik_1 \cdot z - \omega_1 \cdot t)
\overline{E_2} = E_{20} \cdot U_2(x, y) \cdot \exp(ik_2 \cdot z - \omega_2 \cdot t)
\omega_2 = 2\omega_1$$

$$\frac{d}{dz} E_1 = -i\omega_1 \sqrt{\frac{\mu_0}{\varepsilon_1}} \cdot DE_2 E_1^* \cdot \exp[-i(2k_1 - k_2)z]
\frac{d}{dz} E_2 = -i\omega_2 \sqrt{\frac{\mu_0}{\varepsilon_1}} \cdot \frac{1}{2} DE_1^2 \cdot \exp[+i(2k_1 - k_2)z]$$

Phase matching condition

• Only when $2k_1 = k_2$ will SHG be efficient $\Box n(\lambda_1) = n(\lambda_2)$



~ 100% SHG conversion efficiency is possible by optimizing phase matching!

General rule for parametric processes
 SHG, SFG/DFG, THG, FWM
 momentum conservation

Sum frequency generation (SFG) Difference frequency generation (DFG)

- 2nd order optical nonlinearity
- Start with two beams $\omega = \omega_1$ and $\omega = \omega_2$
 - \Box SFG: $\omega_3 = \omega_1 + \omega_2$, $k_3 = k_1 + k_2$
 - $\Box \text{ DFG: } \omega_3 = \omega_1 \omega_2 \text{ , } \text{ } \text{k}_3 = \text{k}_1 \text{k}_2$

SFG/DFG for photodetection

 Use a 1060 nm laser to convert 10 µm mid-infrared radiation to 960 nm near-infrared radiation that can be handled by low-cost detectors



Optical Kerr effect Third harmonic generation (THG)

- 3rd order optical nonlinear effects
- 3rd order optical nonlinearity is present in all materials

Total electric field: $\overline{E} = E_{light} = \text{Re}[E_0 \cdot \exp(i\omega \cdot t)]$

Optical Kerr effect: light-induced refractive index change

 $P_{NL} = \chi^{(3)} \cdot E^3 \sim \chi^{(3)} \operatorname{Re}[3E_0^2 E_0^* \cdot \exp(i\omega \cdot t)] \qquad \text{Consider only the } \omega \text{ terms}$

 $I_0 \propto |E_0|^2 = E_0 E_0^* \implies \Delta n = n_2 I_0 \propto I_0 \implies$ Change of the maginary part of nonlinear index: two photon absorption

Third harmonic generation (THG): frequency tripling $P_{NL} = \chi^{(3)} \cdot E^3 \sim \chi^{(3)} \operatorname{Re}[E_0^3 \cdot \exp(i3\omega \cdot t)]$ Consider only the 3 ω terms

Two photon absorption (TPA)

Bimolecular process

- Absorption depends quadratically on light intensity
- \square Absorption coefficient $lpha_{TPA} \propto I_0$

Resonant enhancement of nonlinear index n₂

□ TPA enhanced near $E_{light} = E_g/2$

- Superior spatial confinement of photo-physical and photochemical reactions
 - 3-d patterning using TPA-induced polymerization





Stimulated Raman scattering (SRS)

- 3rd order optical nonlinearity
- Scales with pump light intensity
- Interaction of photons with phonons
 - Photon phonon = Stokes line
 - Photon + phonon = anti-Stokes line



Stimulated Raman scattering (SRS)

Amorphous materials typically have broad Raman peaks Phonon energy dispersion

• Heavy atoms \rightarrow low phonon energy \rightarrow small Raman shift



Self-focusing and filamentation

- Higher refractive index at beam center due to the high optical intensity: selfsustained waveguiding
- Stand-off detection
 - Unknown substances are identified at a safe distance
 - Sensing approach: Raman
 - High optical intensity required: *pulse-induced filamentation of air*
 - Efficient collection of noncoherent light signal?





Si Raman lasers that make the headline

First silicon laser pulses with life

naturenews

Silicon lasers bring us closer to chips that can process light.

© Getty



- Gain: Raman amplification
- Loss: free carrier absorption due to TPA
- Solution 1: pulsed operation
 - □ Pulse width << $\tau_{carrier}$ << pulse period

O. Boyraz and B. Jalali, "Demonstration of a silicon Raman laser," Opt. Express 12, 5269 (2004).

Si Raman lasers that make the headline

- A continuous-wave Raman silicon laser
- Loss: free carrier absorption due to TPA
- Solution 2: reverse biased p-i-n diode
 - □ Sweep out free carriers due to TPA



H. Rong et al., "A continuous-wave Raman silicon laser," Nature 433, 725 (2005).

Phenomenology of the non-linear optical effects

$$\vec{P}_{i} = \vec{P}_{i}^{L} + \vec{P}_{i}^{NL} = \alpha_{ij}E_{j}^{(\omega)} + \beta_{ijk}E_{j}^{(\omega)}E_{k}^{(\omega)} + \gamma_{ijkl}E_{j}^{(\omega)}E_{k}^{(\omega)}E_{l}^{(\omega)}$$

$$\vec{P}_{i}^{L} = \alpha_{ij} E_{j}^{(\omega)}$$
$$\vec{P}_{i}^{NL} = \beta_{ijk} E_{j}^{(\omega)} E_{k}^{(\omega)} + \gamma_{ijkl} E_{j}^{(\omega)} E_{k}^{(\omega)} E_{l}^{(\omega)}$$

1.1

1.2

where $\alpha_{ij}, \beta_{ijk}, \gamma_{ijkl}$ are microscopic susceptibilities in microscopic case (hyperpolarizabilites) which are related with macroscopic susceptibility χ_{ijk} by equations:

$$\chi_{ij}^{(\omega)} = L_i^{(\omega)} L_j^{(\omega)} \alpha_{ij} \qquad \chi^{(\omega)}_{ijk} = L_i^{(\omega)} L_j^{(\omega)} L_k^{(\omega)} \beta_{ijk} \qquad \chi^{(\omega)}_{ijkl} = L_i^{(\omega)} L_j^{(\omega)} L_k^{(\omega)} \lambda_{ijkl}^{(\omega)} \beta_{ijkl} = L_i^{(\omega)} L_j^{(\omega)} \lambda_{ijkl}^{(\omega)} \beta_{ijkl} = L_i^{(\omega)} \lambda_{ijkl}^{(\omega)}$$

where *i*, *j*, *k* are components of the local Lorenz field, $L_{i,j,k}$ -Lorenz field factors.

Microscopical aspects of the photoinduced NLO changes

Using the oversimplified expression one can present the microscopic hyperpolarizabilities

as:

$$\alpha_{ij} \cong \frac{\overrightarrow{\mu}_i \overrightarrow{\mu}_j}{E_g^2} \qquad \beta_{ijk} \cong \frac{\overrightarrow{\mu}_i \overrightarrow{\mu}_j \, \Delta \overrightarrow{\mu}_k}{E_g^3}$$

$$\gamma_{ijkl} \cong \frac{\overline{\mu}_i \overline{\mu}_j \Delta \overline{\mu}_k \Delta \overline{\mu}_l}{E_g^4}$$
 1.3

Here $\vec{\mu}_{i,j}$ are transition dipole moments and $\Delta \vec{\mu}_{k,l} = \vec{\mu}_{k,l}^{(ex)} - \vec{\mu}_{k,l}^{(gr)}$ are differences between excited and ground dipole moments. For the proper EOE all the description will be similar as for the β_{ijk} .

The latter term is described by third-order space derivatives of the anharmonic potentials:

$$\gamma_{ijk} = \frac{\partial^3 U}{\partial x_i \partial x_j \partial x_k}$$

1.4

$$U = \frac{1}{2!} \alpha_{ij} x^2 - \frac{1}{3!} \beta_{ijk} x^3 - \frac{1}{4!} \gamma_{ijkl} x^4$$

Orientations of particular glass chromophore

Effective electrooptic or SHG coefficients may be evaluated by estimation of the acentric order parameter -<cos³ θ > using an expression:

$$r_{ijk} = 2\beta_{ijk}N < \cos^3\theta > L_{ijk} / n^2$$

$$<\cos^3\theta>=\mu E_{eff}/k_BT$$
 1.6

where *N* is a number of actual LSNC chromophore per volume unit; *n* is effective refractive index.

However, at higher concentration intermolecular interactions *IM* described by an equation (1.7) may be commensurable with the contribution of the intra-chromophore contribution;

$$IM = \mu_{NC} \mu_{pol} / R^3$$
 1.7

Here *R* is a distance between the LSNC possessing state dipole moments μ_{NC} and surrounding polymers with dipole moment μ_{nol} .

Relation between microscopical and macroscopical susceptibilities

The macroscopic second-order non-linear optical susceptibility χ_{ijk} and microscopic hyperpolarisability β_{ijk} are related by expression:

$$\chi_{ijk}^{(\omega,\omega,\omega)} = f_i^{(\omega)} f_j^{(\omega)} f_k^{(\omega)} \beta_{ijk}^{(\omega,\omega,\omega)}$$
^{1.8}

where χ_{ijk} (ω, ω, ω) is a macroscopic second-order optical susceptibility determining the second harmonic generation and Pockels coefficient; $f_{i,j,k}$ (w) – are the *i,j,k* components of the local Lorenz field's factor.

Using an oversimplified two-band model we can present the microscopic hyperpolarizability as described by an expression:

$$\beta_{ijk}^{(\omega,\omega,\omega)} \cong \frac{\vec{\mu}_{gr}^{2} \Delta \vec{\mu}_{tr}(j \to l)}{\left|E_{j} - E_{l}\right|^{4}}$$
1.9

where μ_{gr} is a ground state dipole moments; $\Delta \mu_{gr}(j > l)$ – transition dipole moments between occupied *j* and unoccupied *l* band states.

PRINCIPAL METHODS OF CREATION OF NON-CENTROSYMMETRY



General scheme of the medium polarization for the pure electronic contribution.



Electronic + harmonic electron-phonon contribution.



Electronic + harmonic electron-phonon + anharmonic electron-phonon contribution.



Principal sketch explaining structure of the LSNC.





Principal scheme of creation photo-aligned non-centro symmetry.

Influence of photothermoannealing on the nanocrystallization







C)





B)

D)

Typical pictures of the optical

poling in organic chromophore embdded within the PMMA matrix

obtianed by polarized light at different pump powers:

A) 0.2 GW/cm²;

- B) 0.45 GW/cm²;
- C) 0.65 GW/cm²;
- D) 1.0 GW/cm².

PRINCIPAL SCHEMAT OF OPTICAL POLING



IR-TREATMENT OF NANOCOMPOSITES



PRINCIPAL SET-UP FOR PHOTO-INDUCED ELECTRO-OPTIC MEASUREMENT





Photoinduced optical SHG for the 1540 nm Er-glass lasers after 3-5 min. treated samples in PMMA matrices.

THE EXPERIMENTAL SET-UP FOR THE MEASUREMENT OF INDUCED CHANGES IN THE REFRACTIVE INDEX (Δn)





Photoinduced beam profile distribution of the photocreated crystalline phase

Dependences of the Kerr coefficients in 10⁻¹² m V⁻² versus temperature



PHOTOINDUCED SURFACE TREATMENT OF THE



A)





B)

AFM images of the organic-inoraganic NCA) before the UV laser treatment,B) after 500 pulses of the nitrogen 337 nm lasers,

C) after 1500 pulses of the lasers.

PHOTOINDUCED CHANGES OF ELECTROOPTCS TRANSPARENCY IN CNW



Laser induced changes of the optical absoprtion



Set-up







Photoinduced polarimetry







Dye laser



- **1.** For hybrid organic/ionorganic NC principal role for the non-linear optical effects play the charge density gradients of particular strucutral clusters determining the larger charge transfer and electron-phonon anharmonic interactions;
- 2. To achieve an enhancement of the nonlinear optical effects it is crucial to have a metastable state of the NC composites near the phase transformation or critical points;
- 3. The main restraining factor is increasing light scattering of the nano (micro crystallites and their aggregation, and space disordering of the nanoparticles).
- 4. To achieve the space alignment we need long-range space orientation of the NLO-active chromophore which may be achieved by the thermal poling in the electric field; optical poling by two bicolor cohrent beam, single beam induced microcrystallinity due to local thermoheating causing the local additional non-centrosymmetry on the borders nanocrystallite-polymer, electron beam poling.
- 5. There are two possible regime of the photoinduced changes in the real time when the pumping and probing beams are temporary synchronised and the second one after the irreversible changes, which remain after the switching off of the external fields. As a consequence occurrene of the grating would play here dominant role.
- 6. Role of the local overheating, themodiffusion, thermoexpansion etc. and the appeared coherent phonons plays here substantial role.

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