Liquid Crystal Optical Meta-matertials

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Liquid Crystals for very Broadband Optical Applications

400 nm – 12 microns – Terahertz - Microwave

Molecular structures of liquid crystals and their broadband birefringence.


Samble - Microwave Region,” Liquid Crystals, 30, pp599–602 [2003]

Crossland, Coles, Collings….et al http://www-g.eng.cam.ac.uk/photonics
Other ‘Unique’ advantages of liquid crystals
- Scattering loss $\sim \lambda^{-2.39}$
- Much lower loss for infrared application (e.g. 1.55 $\mu$m communication wavelength)
- Laser hardened - 100's KW cw laser; 10's GW/cm² ns

Contents

• Individual and Collective Molecular Processes
• Optical Dielectric Constant and Refractive Indices
  – Molecular electronic response of individuals [Quantum Mechanics]
  – Collective Effective responses of metamaterials [Electromagnetic Wave Equations]
• Two Possible Routes to LC metamaterials
• Survey of nonlinear optical processes and recent results in LC
Motivations:

1. Design and create new materials with unique and useful functionalities and emergent properties so that the materials will enable new processes or vastly improve current performance of switches, filters, imagers, sensors, and sensor protection devices....etc

2. Learn new physics, chemistry, nano-technologies,

3. Materials with index ~1 and low loss will be very useful
   New material design guidelines, compact high performance devices, ..... so on
Meta-materials - Design and Engineering Real and Imaginary Parts of

\[ \varepsilon (\omega_1, \omega_2, \omega_3...) = \varepsilon' (\omega') + i\varepsilon'' (\omega') \quad \text{and} \quad \mu (\omega') = \mu' + i\mu'' \]

so that \( n = (\mu\varepsilon)^{1/2} \) can be <1, 0 or <0

Tuning of the material enabled by the electro-optics and/or nonlinear optical response of one of the constituents.
Chemical synthesis and molecular engineering to provide new functionalities – extending bandwidth of response

Potential function dictates the energy levels

\[ \varepsilon \sim \varepsilon (\rho_{ii} - \rho_{jj}; d_{ij}); \mu \sim \mu_o \]

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + V_{ext}(\vec{r}, t) - i\hbar \frac{\partial}{\partial t} \right) \Psi(\vec{r}, t) = 0
\]
Absorption spectrum (ground state) of some organic Liquid and Liquid Crystals

[Graph showing absorption spectrum for different materials: ILC, L34, CE9, CE10. Key features include:
- Absorbance (cm$^{-1}$) on the y-axis.
- Wavelength (nm) on the x-axis.
- Multiple peaks across the spectrum.
- Broadband Limiting Application: 400 nm – 900nm.
- Multiple-Time-Scale (fs - ps - ns - μs - ms - cw).
- 1mm cell.]

"Inset graph showing enlarged view of the absorption spectrum for ILC, L34, CE9, CE10 materials."
New neat Nonlinear optical organic liquids quantum molecular energy levels calculation

DPY1: diphenyl acetylene
DPY1-L34: 4-propyl 4’-butyl diphenyl acetylene
DPY2: 1,4-diphenylbutadiyne
DPY2-L44: 4,4’-butyl 1,4-diphenylbutadiyne
DPY3: 1,6-diphenylhexatriyne
Modeling of 2-photon excited state chemical dynamics
e.g. tolane (diphenylacetylene) [L34 like molecules]

1. The calculations were performed using TD-DFT method. The relevant molecular orbitals for ground state \( ^1\text{Ag} \) are listed below.

\( \pi \)-type Occupied Orbitals

- HOMO (b3u)
- HOMO-1 (a1u)
- HOMO-2 (b1g)
- HOMO-3 (b2g)
- HOMO-4 (b2u)

\( \pi \)-type Unoccupied Orbitals

- LUMO (b2g)
- LUMO+1 (b1g)
- LUMO+2 (a1u)
- LUMO+3 (b3u)
- LUMO+4 (b2u)
Excited State absorption of neat liquid DPY1-L34 containing DPY2-L44

\( \lambda_{\text{exc}} = 410 \text{ nm} \)

\( \lambda_{\text{exc}} = 480 \text{ nm} \)

Observed peaks at 410 nm and 480 nm are in agreement with theoretical calculations for DPY1-L34 and DPY2-L44. Transient excited state measurements at PSU and WPAFB [to be published]
Chemical synthesis and molecular engineering + intermolecular correlations → liquid crystalline phases with emergent properties otherwise absent in the constituents molecules

Self-organization via local and long-range order (molecular correlations) — usually non-polar arrangement of dipoles
Liquid Crystal Optical Metamaterials - ‘dispersion engineering’ for emergent “unconventional” optical properties

Conventional Wisdom:
Vacuum $n = 1$
Materials: $n > 1$ ; $n > 0$

Meta-materials:
Appropriate ‘combining’ of material constituents of dielectric constant $\varepsilon_i(r)$
and creating effective dielectric constant $\varepsilon_{\text{eff}} \sim \varepsilon_{\text{eff}} \{\varepsilon_3, \varepsilon_2, \varepsilon_1, \mu^\prime\}$
Avd Permeability $\mu_{\text{eff}} \sim \mu_{\text{eff}} \{\varepsilon_3, \varepsilon_2, \varepsilon_1, \mu^\prime\}$

Resulting in refractive index that could range from sub-unity to below zero
$n = (\mu_{\text{eff}}\varepsilon_{\text{eff}})^{1/2} \{ >1, <1, =0, <0 \}$
Liquid Crystal Optical Metamaterials - ‘dispersion engineering’ for emergent “unconventional” optical properties

- LC + nano-particles


- LC in nano-structures
  - Photonic crystals
  - Frequency Selective Surfaces

Liquid Crystals’ Optical Metamaterials

Details! [or some of the details]

- ‘Assemblies’ of nano-size materials and structures + liquid crystal nano-structures
- Liquid crystal in nano-structures
Nano-Dispersed Liquid Crystals [NDLC] for Electro-Optical and Nonlinear Optical NIM-ZIM and LIM

NDLC - Aligned nematic liquid crystal containing nano-coated-spheres

**Effective Medium Theory**

Response of a Nano-sphere Dispersed Liquid Crystal (NDLC)

Core - Polaritonic Material Response (LiTaO₃):

\[
\varepsilon_1 = \varepsilon(\omega) \left( 1 + \frac{\omega_p^2}{\omega_r^2 - \omega^2 - i\gamma_1 \omega} \right)
\]

Shell - Drude material

\[
\varepsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_2 \omega}
\]

Host - Birefringent nematic liquid crystal (NLC):

\[
\varepsilon_3 = \frac{\varepsilon \varepsilon_\perp}{\varepsilon \cos^2 \theta + \varepsilon_\perp \sin^2 \theta}
\]

Effective permittivity

\[
\varepsilon^{\text{eff}} = \varepsilon_3 \left( \frac{k_3^3 + j4\pi Na r}{k_3^3 - j2\pi Na r^3} \right)
\]

Effective permeability

\[
\mu^{\text{eff}} = \frac{k_3^3 + j4\pi Nb r^3}{k_3^3 - j2\pi Nb r^3}
\]

\[
k_3 = \sqrt{\varepsilon_3 k_0} = \left( \frac{\varepsilon \varepsilon_\perp}{\varepsilon \cos^2 \theta + \varepsilon_\perp \sin^2 \theta} \right)^{1/2} k_0
\]

Nano-Dispersed Liquid Crystals [NDLC]
Tunable NIM-ZIM and LIM

** Challenges of current work: **
Volume Fraction; Loss
Photonic Crystals-Dispersed Liquid Crystalline Metamaterials
Liquid Crystal Infiltration

- Hydrophilic (untreated) samples
  - Infiltrated with pure 5CB at 50°C.
  - Drop at gap of the sample cell.
  - Immediate color change.

- Hydrophobic (treated) samples
  - Infiltrated with a mixture of 5% 5CB in ethanol at 20°C.
  - Drop at edge of partially open cell.
  - Gradual color change with repeated application
  - Post infiltration ensured ethanol removal.
Electric Field Tuning: 
TiO$_2$ Large-pore inverse shell opals

- Reflectance spectra for increasing applied electric field (bipolar square wave at 1 kHz) for 2 large-pore samples.

Hydrophobic treated

Hydrophilic

Periodic Metallo-Dielectric Structures

Frequency Selective Surfaces

Introducing electro-optical and all-optical tuning and modulation capabilities with the incorporation of liquid crystals

Utilizing the broadband and Large Birefringence and Nonlinearity of liquid crystals for low power threshold and broadband [optical – microwave] application
(Conventional) FSS - Introduction

- AC Current induced on metal at wavelength resonant with periodic geometry
- Surface looks like solid perfect electric conductor at this wavelength
- Energy at this wavelength reflected

- Frequency response scales with element dimensions
  - FSS designs developed at microwave and RF can be adapted to IR and visible by using micro- or nanofabrication to scale the dimensions
All-Dielectric FSS with Liquid Crystal Tunable Superstrate

Unit Cell of DFSS – side view

Latest (7/14/2008) Results (Feasibility of Optical tuning in very thin sample):

Observed degenerate four wave mixing in 250 nm thick dye-doped liquid crystals. Diffraction efficiency corresponds to an index change of $\sim 0.1$

Feasibility of Optically Tunable Nano-structured Meta-materials!
Optical tuning of Meta-materials
Optical Nonlinearity of Liquid Crystals

\[ n_2 \sim (n_e - n_o) \tau(\eta \alpha) \Lambda^2 / K \]

\( \tau \sim 10^{s} \) of millisecond (10\(^{-2}\) sec) – depends on \( \eta \) viscosity, elastic constant \( K \), characteristic modulation length \( \Lambda \), efficiency of energy transfer \( (\alpha \eta) \)

\[
\begin{align*}
\Lambda & \sim 20 \, \mu m, \, K \sim 10^{-7}, \, (n_e - n_o) \sim 0.2, \, \eta \alpha \sim 100 \, \text{cm}^{-1} \\
n_2 & \sim 16 \, \text{cm}^2/\text{W} \quad [10^5 \text{ - } 10^{12} \text{ times other materials}] \\
& \quad \text{[Khoo et al]} \\
\Lambda & \sim 100 \, \mu m, \, K \sim 10^{-7}, \, (n_e - n_o) \sim 0.5, \, \eta \alpha \sim 100 \, \text{cm}^{-1} \\
n_2 & \sim 1000 \, \text{cm}^2/\text{W} \quad \text{[Simoni et al]} 
\end{align*}
\]

Require very small optical intensity to trigger effect

\( mW, \mu W \text{ and } nW \text{ nonlinear optics} !! \)

Compatibility with other optoelectronic materials makes liquid crystals the preferred material of choice for tunability [electro-optical or all-optical]
“All” nonlinear optical processes have been observed in liquid crystals

- Harmonic generations [2\textsuperscript{nd}, 3\textsuperscript{rd}, ...etc]
- Self-focusing, defocusing, phase modulation, ... self action effects
- Optical Wave Mixings, phase conjugations, transient and steady state, beam coupling, self-starting ...
- Stimulated scatterings, SOS, SBS, STS, ...

Purely Academic Applications
## Recent Publications


1550 nm cw – μs optical limiting [TE or TM]

\[ P(\phi) = \begin{pmatrix} \cos^2 \phi & \cos \phi \sin \phi \\ \sin \phi \cos \phi & \sin^2 \phi \end{pmatrix} \]

\[ S(\phi_m) = \begin{pmatrix} \cos \phi_m & \sin \phi_m \\ -\sin \phi_m & \cos \phi_m \end{pmatrix} \]

\[ G = \begin{pmatrix} e^{\frac{\gamma L}{2}} & 0 \\ 0 & e^{-\frac{\gamma L}{2}} \end{pmatrix} \]

\[ \gamma = \frac{2\pi h \Delta n_m}{\lambda} \]

\[ \Delta n_m = \frac{n_x n_o}{\sqrt{n_x^2 \sin^2 \theta_m + n_o^2 \cos^2 \theta_m}} - n_o \]

\[ \Psi_{\text{out}}(d) = \left[ \begin{array}{c} E_x' \\ E_y' \end{array} \right] = P(\phi_{\text{Exit}}) \cdot \prod_{m=1}^{M} \left[ S^{-1} (\phi_m) \cdot G \cdot S (\phi_m) \right] \cdot \begin{pmatrix} \cos \phi_{\text{Exit}} \\ \sin \phi_{\text{Exit}} \end{pmatrix} \]

Very Broadband [400 nm – 1550 nm; abd beyond - ....to 12 μm]
cw – μs optical limiting/switching application

- 400 nm – 12 microns
- Clamped Transmission <MPE
- Dynamic Range > 10³ [> 26 db extinction]


Recent Results: (81mW), 30um TN sample, MR-5CB 0.5%wt

Possible to have nanoseconds response speed
  e.g. Laser induced order-parameter changes, T. Ikeda and A. Shishido et al, J. Am. Chem. Soc. 119 pp. 7791-7796 (1997)]
Previous Results: (81mW), 30um TN sample, MR-5CB 0.5%wt

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