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Title: HYBRID ORGANIC-INORGANIC PHOTOREFRACTIVES (Preprint)

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Abstract:
Surface space charge field modulates the local liquid crystal alignment. Liquid crystals amplify the refractive index modulation. Highlights the opportunity of exploiting the electric field sensitivity and large birefringence of liquid crystals.

Subject Terms:
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Hybrid Organic-Inorganic Photorefractives

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A Perfect Marriage

Solid Crystals

Liquid Crystals
Photorefractive material

- Concept and theory
- Surface space charge field modulates the local liquid crystal alignment
- Liquid crystals amplify the refractive index modulation
- Highlights the opportunity of exploiting the electric field sensitivity and large birefringence of liquid crystals
Polymer Version

- Very high gain coefficient, but.......  
  - Small grating phase shift (drift dominated charge migration)  
  - Applied fields  
  - Tilted optical geometry  
  - Small beam intersection angles (low trap density) - Raman-Nath regime only

Inorganic-Organic Hybrids

- Space charge field is governed by the inorganic crystal properties  
- 90 degree grating phase shift possible  
- Normal incidence operation  
- No applied fields - entirely passive device  
- Large beam intersection angles (trap density) - Bragg regime possible
Problems with photovoltaic beam fanning
Charge migration is dominated by the photovoltaic effect (drift)
Phase shift is poor unless space charge field saturates (difficult at coarse grating spacing)

BSO/BGO
- Very sensitive and high speed
- Excellent charge diffuser and photoconductor
- Optically active

Fe:KNbO₃ and SPS
- Very sensitive and high speed (Fe/Ni/Ag etc. KNbO₃ and Te:SPS)
- Good charge diffusers and photoconductors
- Maybe difficult to obtain in large sizes (but we're working on that!)
- Relatively small (KNbO₃) or near zero (SPS) photovoltaic effect

Ce:SBN
- Quite sensitive
- Charge migration is dominated by diffusion - phase shift approaches 90 degrees
- No complications from photovoltaic effects

### Inorganic Choices

- Fe:LiNbO₃
  - Inensitive
  - Problems with photovoltaic beam fanning
  - Charge migration is dominated by the photovoltaic effect (drift)
  - Phase shift is poor unless space charge field saturates (difficult at coarse grating spacing)

### Organic Choices

- Lots!
  - Homeotropic
  - Planar
  - Twisted
  - Bend
  - Splay
  - Planar/homeotropic

- 100's of possible liquid crystals, many possible phases
  - Nematic
  - Smectic
  - Ferroelectric

- Probably best to avoid ionic liquid crystals
  - Possible screening charge problems
  - Fluorinated liquid crystals look good
Outline Theory (SBN)

- **Intensity fringes**
  \[ I(y) = \left( I_{\text{signal}} + I_{\text{pump}} \right) \left( 1 + \frac{A_{\text{pump}} N_{\text{eff}}}{I_{\text{signal}} + I_{\text{pump}}} \right) \cos \left( 2k \sin(\theta) y + \phi \right) \]

- **Space charge field**
  \[ E_x = \frac{i E_0}{1 + E_0 / E_0} \]
  \[ E_x = \alpha N_{\text{eff}} \]
  \[ N_{\text{eff}} = \frac{\sqrt{\pi} I_0}{(2 \pi)^{3/2}} \]
  \[ m = \frac{2 \sqrt{\pi} I_0}{I_{\text{signal}} + I_{\text{pump}}} \cos \left( 2 \theta \right) \]

- **Exponential gain coefficient**
  \[ \Gamma = \frac{2 \pi}{\lambda} n' r'_0 \text{Im}(E_x) \]

  \[ r_0 = r_0 \cos^2(\theta - \epsilon_x) \sin^2(\theta + \epsilon_x) \]

- **Electrostatic potential**
  \[ V(x, y) = \frac{1}{2} E_x \left[ i K y - K x \right] + \text{c.c.} \]

Outline Theory (Liquid Crystal)

- **Electric torque**
  \[ F_x = \Delta \chi (\hat{e} \times \mathbf{E}) \]

- **Elastic torque**
  \[ F_x = \hat{e} \times (E_1 + E_2 + E_3) \]

- **Refractive index modulation**
  \[ n = \frac{n_0}{\sqrt{n_0^2 \sin^2(\beta \pm \theta) + n_s^2 \cos^2(\beta \pm \theta)}} \]

  where \( n_0, n_s, \text{and} E \) are the molecular fields associated with bend, splay, and twist deformations respectively.

- **Steady state molecular reorientation is achieved when** \( E_x = F_x \)

- **Space-charge field penetrates -1.5 - 2.0x grating spacing**

- **Intermolecular elastic forces permit longer range influence**
Preliminary Cell Construction

Optional electrode connections

12.5um Copper foil

Liquid crystal

SBN crystal windows

Bulldog ® stationery clips


Cell Preparation
Preliminary Experiments


Works!
Preliminary Results with Nematics

- Works! ← but it should not have worked!
- Full Bragg matching
- 90 degree grating phase shift
- Sensitive to alignment (Etalon effects)


Molecular Alignment Issues

- Glass test cells show no pre-tilt, so the symmetry should not be broken
- Needs a broken symmetry and a molecular polarity to work
New Results
C-parallel Nematic Cell

- Clear indication of a pre-tilt and the flexoelectric effect
- Pre-tilt is larger in the negative c-axis direction
- Pre-tilt direction follows rubbing direction

C-parallel Nematic Cell Dynamics

- Van der Waals forces from crystal induce a pre-tilt
- Pre-tilt provides the required molecular asymmetry
- Flexoelectric effect provides molecular polarity
- Space-charge field molecular rotation is out of plane

Large positive gain  Small positive gain  Moderate negative gain

New Results
C-orthogonal Nematic Cell

Planar TL205, orthogonal to the c-axis/0.01%Cs:SSN Hybrid Cell

- Clear indication of a pre-tilt and the flexoelectric effect
- Pre-tilt is larger in the “up” direction
- Pre-tilt direction is independent of the rubbing direction

C-orthogonal Nematic Cell Dynamics

- Space-charge field molecular rotation is an in-plane twist

Rub
Up - up
Rub
Up - down
Rub
Down - down

Large positive gain Moderate positive gain Small positive gain
New Results
Homeotropic Nematic Cell

- Clear indication of a pre-tilt and the flexoelectric effect
- Low gain implies a small pre-tilt with bend rather than splay alignment

Having identified a crystal substrate induced pre-tilt, choose alignment schemes to maximize this effect........
Pre-tilt direction and magnitude depends on the c-axis rubbing direction but gain always remains positive so homeotropic layer dominates cell alignment slightly better with a negative rub, homeotropic layer is therefore pre-tilted towards the negative c-axis.

Pre-tilt magnitude (not direction) depends on the up/down rubbing direction. Homeotropic layer is pre-tilted towards the negative c-axis (previous slide). Gain always remains negative, no difference between up or down rub (homeotropic dominates). Combination of orthogonal pre-tilts gives a twisted hybrid alignment.
Twisted Nematic Cell

Twist direction is constant (a-axis rub direction changes just the pre-tilt magnitude)
- Smaller pre-tilts reduce the twist “tension” and the flexoelectric effect
- Positive c rub has smaller pre-tilt than negative c rub, so gain is increased
- Pre-tilt is larger in the “up” direction, so gain is less for “up” rubbed cells
Pre-tilt Summary

- C-parallel planar: bidirectional c-axis pre-tilts, largest for negative c rub
- C-orthogonal planar: unidirectional a-axis pre-tilt, largest for "up" rub
- Homeotropic: c-axis pre-tilt
- Hybrid c-parallel planar/homeotropic: c-axis pre-tilts
- Hybrid c-orthogonal planar/homeotropic: a and c-axis pre-tilts
- Twisted nematic: a and c-axis pre-tilts

Cause?

SBN Crystal structure

Oxygen atoms at the vertices of the polyhedra

occupied by Sr
occupied by Ba or Sr

Crystal structure influences the liquid crystal pre-tilt
Surface poling condition is therefore critical
Typical poling method:

\[
E_1 \neq E_2 \text{ if } \varepsilon_{\text{air}} \neq \varepsilon_{\text{SBN}} \\
E_R \neq 0 \text{ if } E_1 \neq E_2
\]

SBN Poling

Modified poling method:

\[
\varepsilon_{\text{air}} = \varepsilon_{\text{SBN}} \\
E_1 = E_2 \\
E_R = 0
\]
SBN Poling

![Graph showing gain vs. angle between signal and pump for different poling methods.]

Rotated Cell Results

- Liquid crystal gain present only when the grating k-vector has a component along the SBN crystal c-axis

![Graph showing gain vs. grating spacing for different c-axis orientations.]

Rotated Cell Results

- Unexpected result
  - Liquid crystal gain vanishes when SBN c-axis is orthogonal to grating k-vector
    - SBN EO coefficients are zero
  - But the SBN diffusion field is still present!
  - Liquid crystal reorientation not driven directly by the diffusion field?
  - 90° phase shift strongly suggests the modulation mechanism is linked to charge diffusion
    - Piezoelectric?

Piezoelectric Search
Found no evidence (yet) of piezoelectric surface deformations

If piezo effects are absent, LC must be driven by surface fields

Absence of LC beam coupling for k-vector at 90° to c-axis means an absence of a space-charge field

No space-charge field means either:
  - Zero charge diffusion across the c-axis (unlikely)
  - Negligible effective trap density across the c-axis (surprising)
Full Bragg matching for grating spacings of $-400 \text{nm} - 5 \mu\text{m}$.

- $90^\circ$ grating phase shift
- Surface pre-tilt and the flexoelectric mechanisms identified for unidirectional beam coupling
  - c-axis pre-tilt direction and magnitude depends on rubbing direction
    - Pre-tilt is greatest in the negative c direction
    - a-axis pre-tilt magnitude depends on the rubbing direction
  - Homeotropic alignment yields a pre-tilt towards the negative c-axis
  - SBN crystal structure is proposed as causing the pre-tilt through Van der Waal's forces
  - Poling quality is important for unidirectional gain (pre-tilt direction may otherwise vary)
- LC gain present only when a component of the grating k-vector lies along the c-axis
  - No evidence (yet) of piezoelectric induced LC alignment
  - Surface field induced LC alignment
  - No space-charge field for k-vector orthogonal to SBN c-axis – reason is unclear