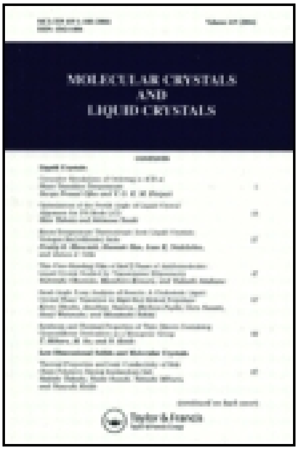

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Substrate Induced Pre-tilt in Hybrid Liquid Crystal/Inorganic Photorefractives

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We report on the photorefractive properties of nematic liquid crystals sandwiched between windows of cerium doped strontium barium niobate (Ce:SBN). Unlike simple glass substrates, the Ce:SBN induces molecular pre-tilts that generate electric dipole moments in the liquid crystal through the flexoelectric effect. This enables the liquid crystal to become sensitive to the sign of the space-charge field and leads to an increase in the optical amplification when the cell thickness is decreased.

Keywords: hybrid; liquid crystal; photorefractives; pre-tilt; surface effects

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INTRODUCTION

For three decades the photorefractive effect has been studied in inorganic electro-optic crystals for applications that rely on an exchange of energy in a variety of non-linear wave-mixing processes [1]. In two-wave mixing, unidirectional transfer of energy allows a weak signal beam to grow exponentially with distance, ultimately limited by the effects of pump depletion. For inorganic crystals the exponential gain coefficient is generally in the range of 10 to 100 cm^{-1}, with the highest observed in iron doped lithium niobate [2]. These gain coefficients are governed by the relatively small modulation in refractive index, approximately 10^{-4}, that is achievable from minute perturbations of the crystal lattice through the electro-optic effect (the linear Pockel's effect). Dielectric breakdown limits the magnitude of the space-charge field enhancements possible through additional contributions from externally applied fields.

In the past few years, spectacular advances of photorefractive-like interactions have been reported in liquid crystal cells. These strong interactions can be seen in thin layers owing to the very high refractive index modulation, typically 0.2, that can be achieved following reorientation of the liquid medium. Gain coefficients as large as 2890 cm^{-1} have been reported using a doped nematic liquid crystal in which the local molecular alignment was modulated using an internally generated space-charge field from photo excitation [3]. In other experiments an undoped nematic liquid crystal was reoriented by photo-generated space charges in adjacent photorefractive [4] or photoconducting layers [5,6], the latter yielding gain coefficients up to 3700 cm^{-1}. This arrangement has been studied theoretically [7,8] and these gain coefficients are two orders of magnitude higher than those typically seen in solid inorganic crystals. Until recently, these advances have been restricted to operation in the Raman-Nath regime, generating multiple order diffracted beams and restricting the angle between the pump and signal beams to less than a few degrees. However, recent work has demonstrated large liquid crystal gain coefficients can be achieved in the Bragg regime when the space-charge field originates from inorganic photorefractive crystals used as windows for undoped nematic liquid crystal cells [9]. In these devices, the grating period is much less than the liquid crystal layer thickness. These cells have become known as hybrid organic-inorganic photorefractives. In such devices the evanescent field from the inorganic window exerts a torque on the nearby liquid crystal molecules. The free energy of a liquid crystal is minimized when the molecules align parallel to adjacent molecules. The electric torque therefore induces an elastic torque in the liquid crystal as the molecules are rotated out of alignment. Steady state modulation of the liquid crystal occurs when the electric torque and the intermolecular elastic torques balance.

Bragg matched amplification is useful for many applications but the origin of optical gain in hybridized devices has been poorly understood. Hybrid photorefractives require two key parameters from the liquid crystal layer; a break in the alignment symmetry of the liquid crystals (e.g., a pre-tilt) and sensitivity to the sign of the space-charge field. Figure 1 illustrates the combined needs of a pre-tilt and electrical polarity in the liquid crystal layer. Without these conditions the alignment of the liquid crystal molecules is symmetric and insensitive to the sign of the space-charge field. The local refractive index change arising from space-charge induced modulation is the same irrespective of the sign of the space-charge field. This results in a refractive index grating with twice the spatial frequency of the optical interference pattern. However, a molecular pre-tilt combined with a molecular electrical polarity allows the local refractive index to rise or fall depending on the sign of the space-charge field. This enables the refractive index grating to have the same spatial frequency as the optical interference

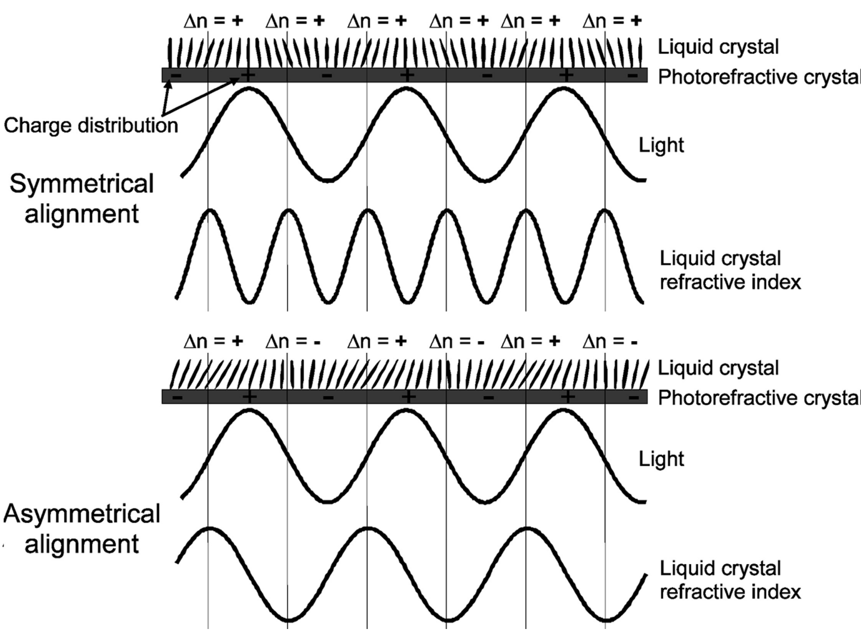

FIGURE 1 Liquid crystal molecular alignment and polarity effects.

pattern and makes Bragg matched optical amplification possible. The difficulty has been in identifying why these conditions exist since nematic liquid crystals are insensitive to the sign of an electric field. In this paper we present experimental results which clearly demonstrate the origin of Bragg matched amplification in hybrid organic-inorganic photorefractives.

EXPERIMENT

Two uncoated inorganic crystals of strontium barium niobate doped with 0.01 weight% cerium (Ce:SBN) were used as windows for the liquid crystal cell. The windows, supplied by Ingcrys Laser Systems Ltd, UK, were optically polished with finished dimensions of $20\,mm \times 20\,mm \times 1.3\,mm$. The crystal c-axis was parallel to one of the 20 mm long edges. The linear absorption coefficient for each window was approximately $0.5\,cm^{-1}$. The crystals were poled in our laboratory to create a single ferroelectric domain by heating each window above the Curie temperature for SBN (approximately 75°C) followed by gradual cooling to room temperature in the presence of an externally applied electric field of $3\,kV\,cm^{-1}$. The designation of positive and negative c-axis faces of poled crystals varies in the literature; to avoid any ambiguity we here define our positive c-axis face to be that corresponding to the positive electrode c-face during poling. In our experiments it became evident that the poling method is a very important parameter for hybrid cell windows. This will be discussed in more detail later in this paper.

Once poled and cleaned, the inside surface of each window was spin coated at 4000 RPM for 30 seconds with either a nylon multipolymer (Elvamide® 8023 R, supplied by DuPont, prepared as a 0.125 weight% solution in anhydrous methanol), or a surfactant (cetyltrimethylammonium bromide, supplied by Aldrich, prepared as a 0.025 weight% solution in anhydrous methanol). After drying at room temperature for approximately 1 hour the nylon coated cells were uni-axially rubbed using a nylon roller rubbing machine supplied by BEAM Engineering for Advanced Measurements Co., FL, USA, to induce a planar alignment of the liquid crystals. The surfactant coated cells produced a homeotropic alignment of the liquid crystals and did not require rubbing. A macroscopic alignment, either planar or homeotropic, was required; uncoated Ce:SBN did not induce any net alignment of the liquid crystals.

After preparation, simple spring stationery paper clips were used to hold the cell together, sandwiching polymer shim-stock spacers between the two windows. One edge was left unsupported to allow the cells to be filled with liquid crystals using capillary attraction. Careful measurements of the filled volume using a μL syringe enabled the cell gap thickness to be confirmed. All of the results reported here were obtained using the eutectic liquid crystal mixture TL205 (Merck), selected for its low ionic impurity levels. Low levels of ionic contamination are important to prevent the build up of screening charges within the cell. Although the space-charge field is spatially periodic, the electric field is essentially D.C. in nature and so the occurrence of screening charges can be problematic. Earlier tests in our cell using a more ionic liquid crystal 5CB (Merck) gave poorer results due to the presence of screening charges.

The experimental arrangement is shown in Figure 2. A 532 nm continuous wave Coherent Verdi® laser together with a 50% reflective beam splitter provided the pump and signal beams. Two 100% reflective mirrors controlled the beam intersection angle, θ, creating an interference pattern in the hybrid cell with a fringe spacing, Λ, given by

$$\Lambda = \frac{\lambda}{2\sin(\theta/2)} \tag{1}$$

where λ is the laser wavelength in air. The pump beam power at the hybrid cell was 10 mW with a 4 mm $1/e^2$ diameter spot size, giving a local peak pump intensity of approximately 160 mW cm^{-2}. Neutral density filters attenuated the signal power to 7 μW, giving a local peak signal intensity of approximately 56 μW cm^{-2} with a spot size identical to the pump beam. The low signal intensity ensured that the net gain for the hybrid cell remained in the small signal regime during the experiment.

The hybrid cell was placed at the overlap of the pump and signal beams and oriented approximately normal to the bisector of the two

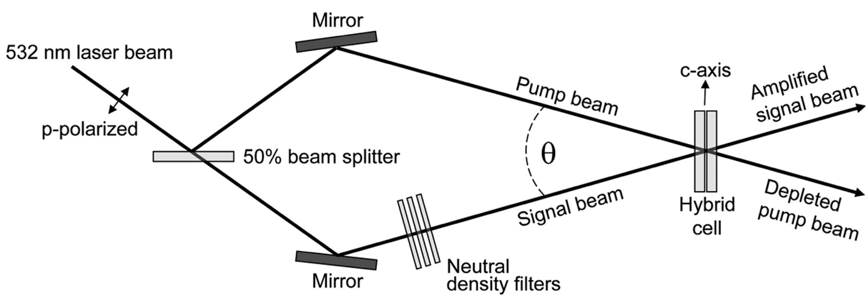

FIGURE 2 Experimental arrangement.

beams with the c-axis of each window in the plane of the incident polarization. The c-axes directions were such that the signal beam was amplified by the Ce:SBN. A power meter (Newport model 2832-C with two model 818SL detectors) was used to monitor the transmitted pump and signal beam powers. The measured gain is defined as being the power of the signal beam with the pump beam present divided by the transmitted signal beam in the absence of the pump beam. There was no scatter detected from the pump by the signal beam detector. Prior to filling with liquid crystal, the gain of the cell was measured at each grating spacing to provide reference gain characteristics of the Ce:SBN windows. To minimize reflection and etalon effects, the cell was filled with oil of a similar refractive index to the liquid crystal TL205 ($n_o = 1.527$) while making these reference measurements. After cleaning and re-processing, the cell was filled with liquid crystal and the gain measurements repeated. For each grating spacing the gain of the liquid crystal was determined by dividing the liquid crystal filled cell gain by the oil filled cell gain. The gain coefficient, Γ, for the liquid crystal is then given by

$$\Gamma = \frac{1}{d}\log_e(G) \tag{2}$$

where G is the small signal gain and d is thickness of the liquid crystal layer.

RESULTS AND DISCUSSION

During initial tests, it became evident that the liquid crystal gain contribution from successive cell assemblies was somewhat haphazard. A correlation appeared between the liquid crystal gain and the apparent arrangement of the windows and/or the rubbing direction. Following this observation, each window and each face was carefully marked to trace the relative assembly parameters between successive cell constructions. The liquid crystal small signal gain was then measured as a function of the rubbing direction with respect to the c-axis, preserving the assembly order and orientation of each respective window between measurements. Figure 3 compares the liquid crystal gain coefficients obtained from a 10 μm thick layer of TL205 with the alignment layers rubbed parallel towards the negative c-axis, anti-parallel, and parallel towards the positive c-axis, respectively. The gain is maximized when the rubbing direction for both windows is towards the negative c-axis, and is much smaller for anti-parallel rubbing. The gain becomes *negative* (i.e., the pump is amplified by the signal) when both surfaces are rubbed towards the positive crystal c-axis.

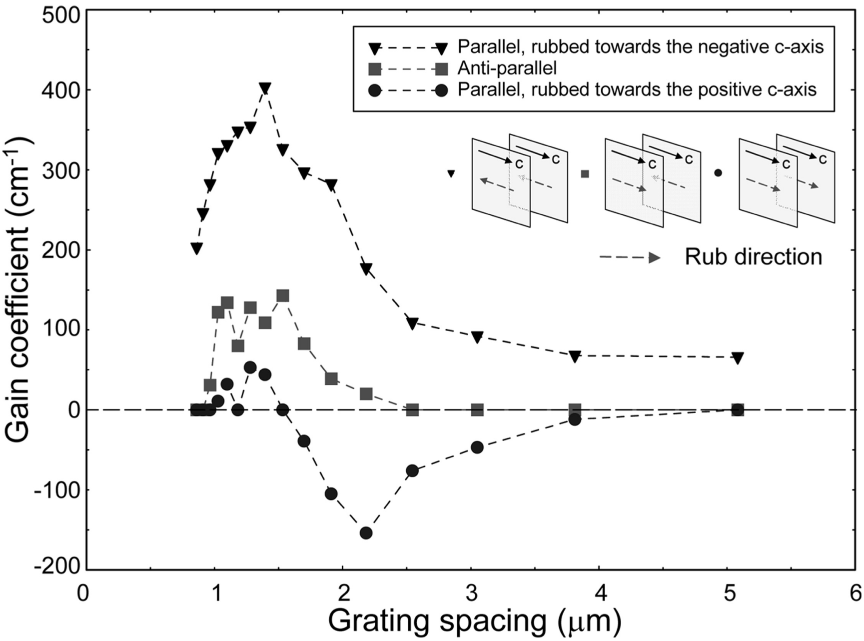

FIGURE 3 c-Parallel rubbed liquid crystal gain coefficients for a 10 μm thick cell containing TL205.

These results immediately indicate the presence of surface pre-tilt effects and, since the magnitude of the gain is highest for parallel rubbing, suggest that the flexoelectric effect [10] is the reason for the sensitivity to the sign of the space-charge field. The flexoelectric effect induces a molecular polarity because parallel rubbing in the presence of a pre-tilt causes the planar aligned molecules to become splayed, squeezing together the ends of the molecules and causing a tiny displacement of the electron cloud in each liquid crystal molecule. Surface pre-tilt effects provide the necessary break in the alignment symmetry and the flexoelectric effect induces an electrical polarity to the liquid crystal molecules, satisfying the conditions shown in Figure 1. This one experiment accounts for the presence of unidirectional gain in hybrid photorefractive devices.

Glass test cells using the same rubbing geometries showed no sign of any pre-tilts, indicating that the origin of the pre-tilt is probably van der Waal's forces from the Ce:SBN windows, and not caused directly by the alignment layer. However, the gain reversal for positive c-axis rubbed windows shows that the rubbing layer does play a role in the pre-tilt process. We note that the gain is largest for negatively rubbed windows, indicating the magnitudes of the pre-tilt and the related flexoelectric effect are greatest for this rubbing direction. Attempts to directly measure the pre-tilt angle using optical methods have so far been unsuccessful. The birefringence of the windows increases the experimental error, but this error allows us to estimate the maximum surface induced pre-tilt to be less than 5°. Similar pre-tilt effects in which the substrate can influence the liquid crystal alignment through the rubbing layer have been reported previously [11].

For all cases, the amplified (or attenuated) signal beam was perfectly Bragg-matched with no sign of any Raman-Nath diffraction, even for equal pump and signal intensities. The gain remained uni-directional irrespective of the relative intensities of the pump and signal beams, confirming the presence of a phase-shifted grating with respect to the interference pattern.

A similar experiment was conducted with rubbing directions orthogonal to the window c-axes. For these measurements, rubbing towards the top of the cell was arbitrarily defined as "up" while rubbing in the opposite direction was again arbitrarily defined as "down". Ce:SBN is a uni-axial inorganic crystal and so it was surprising to discover that there were differences in the liquid crystal gain as a function of the "up" and "down" rubbing directions orthogonal to the c-axis. In Figure 4 we see the small signal gain coefficient for TL205 is maximized for parallel rubbing in the "up" direction and drops significantly for parallel rubbing in the "down" direction. Anti-parallel rubbing produces an intermediate gain value. Unlike the case for c-axis rubbing, the gain remained positive, showing the pre-tilt direction was independent of the rubbing direction, but the magnitude of the pre-tilt was affected by the rubbing conditions. As before, beam coupling remained unidirectional, irrespective of the relative intensities of the two beams, and entirely Bragg matched. The peak gain coefficient occurred at a grating spacing of approximately 1.5 μm, close to the optimum grating spacing for beam coupling in Ce:SBN where the space-charge field is largest.

An analogous pre-tilt behavior was also found for homeotropically aligned cells. Figure 5 shows the liquid crystal small signal gain for TL205 as a function of grating spacing. The gain characteristics are similar to the planar alignments, although the gain is somewhat less than the peak values obtained with the rubbing layers. The presence of unidirectional gain shows the homeotropic alignment is pre-tilted away from normal, but the reduced gain implies the pre-tilt deviation from normal is a little less than the planar pre-tilt angle. Given the small deviation from normal, it is likely the homeotropic cell is dominated by a bend, rather than a splay alignment.

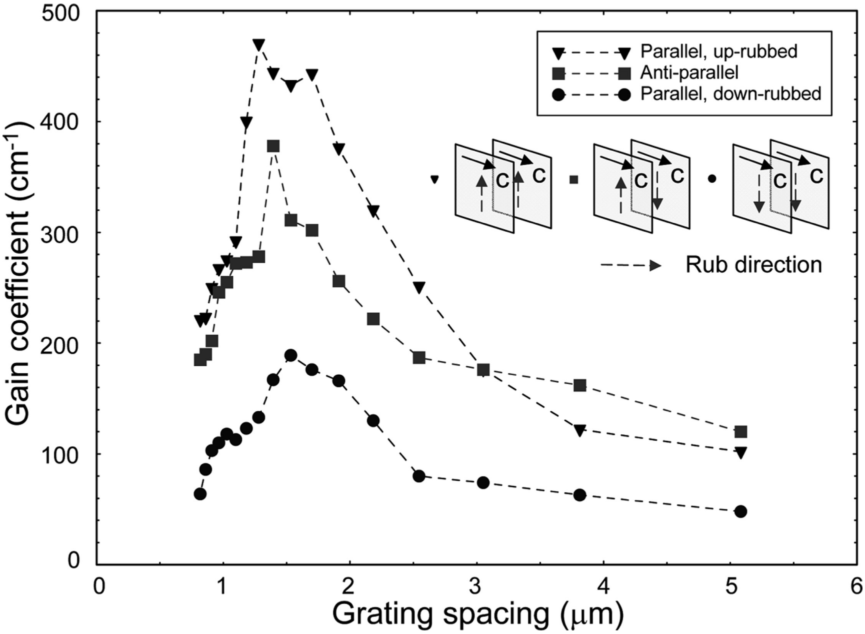

FIGURE 4 c-Orthogonal rubbed liquid crystal gain coefficients for a 10 μm thick cell containing TL205.

An interesting characteristic of hybrid photorefractive cells is the gain variation with cell thickness. We have found the optical gain *decreases* as the liquid crystal thickness *increases*. Figure 6 compares the small signal gain as a function of grating spacing for liquid crystal cell thicknesses of 10 μm, 20 μm, and 38 μm. We attribute this curious behavior to the flexoelectric effect. For any given alignment arrangement, the surface molecular pre-tilt is constant and independent of the liquid crystal thickness. For parallel rubbing, the relative molecular splay between adjacent molecules across the cell spacing will be larger for thinner cells than for thicker cells. The flexoelectric induced polarity will therefore be greatest when the cell spacing is small. Thicker cells should be less sensitive to the space-charge field than thinner cells. The net *gain*, as well as the gain coefficient, increases when the cell thickness is decreased. This is an unusual characteristic for an optical amplifier as it is more common for the amplification to diminish if the gain medium path length is reduced. The thickness dependent gain also proves that the gain originates in the liquid crystal layer and that the liquid crystal is not somehow enhancing the space-charge field or electro-optic effect in the Ce:SBN windows.

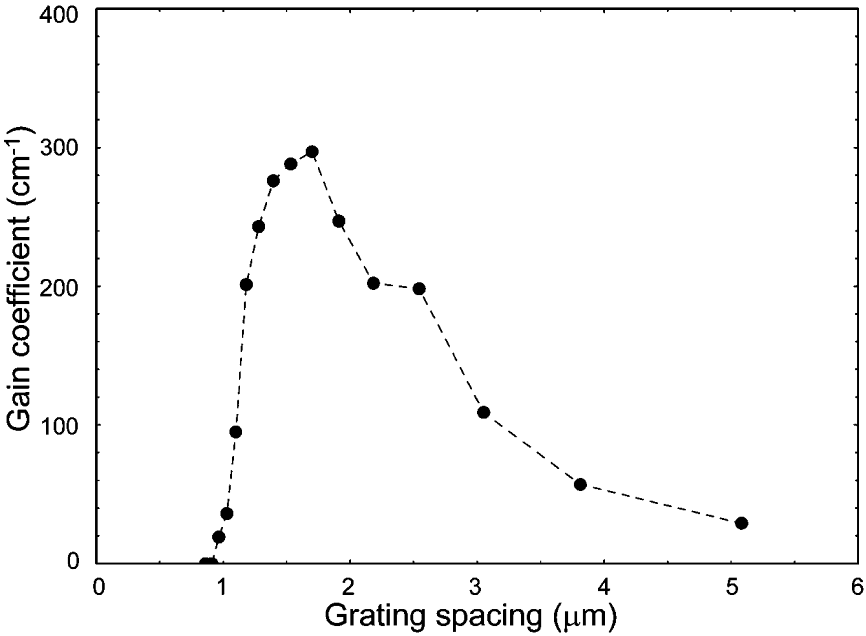

FIGURE 5 Homeotropic crystal gain coefficients for a 10 μm thick cell containing TL205.

The surface induced pre-tilt clearly originates from the Ce:SBN windows but it is uncertain how the Ce:SBN exerts a directional preference to the pre-tilt. A clue comes from the crystal structure of SBN, which belongs to the tungsten-bronze class of crystals and has a tetragonal structure at room temperature [12]. The principal crystal axes are aligned parallel to the loci between strontium ions at the corner of the unit cell structure [12,13]. However, the oxygen sites occupy a complex polyhedral structure which is inclined with respect to the a-axis. The a-axis faces are in contact with the liquid crystal and so we propose that the inclined plane of oxygen sites within SBN may be the cause for the directional dependence of the liquid crystal pre-tilt in hybrid photorefractives.

The liquid crystal pre-tilt, and hence the flexoelectric effect and optical gain, depend on how the Ce:SBN influences the local liquid crystal molecular alignment. We have demonstrated that the liquid crystal is sensitive to the direction of the Ce:SBN c-axis. The performance of the hybrid system therefore depends critically upon the quality of the Ce:SBN domain structure. If the crystal is not fully poled, particularly at the surface interface with the liquid crystal, the liquid

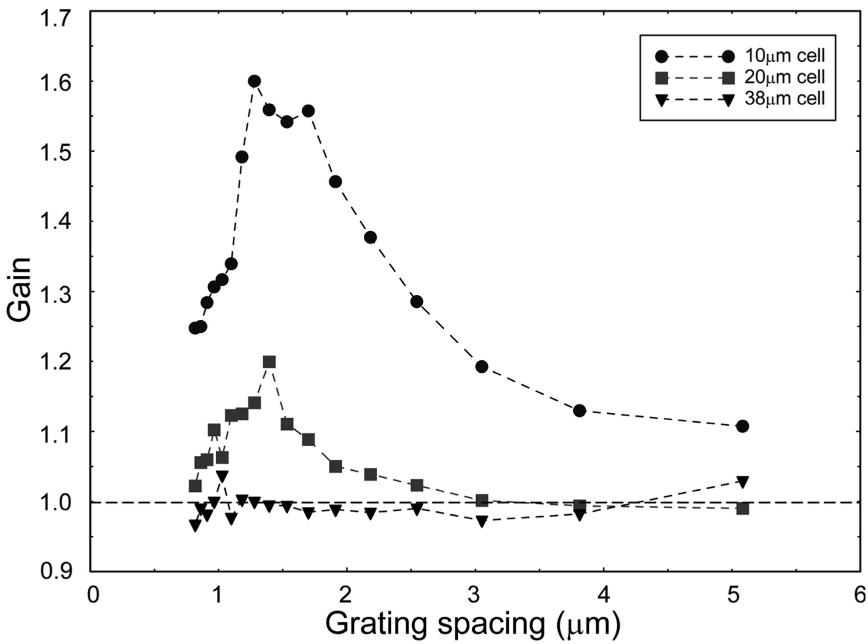

FIGURE 6 TL205 Liquid crystal gain as a function of cell thickness for parallel "up" rubbed alignment orthogonal to the c-axis.

crystal optical gain can be greatly reduced. If "islands" of unpoled material exist at the surface, the local pre-tilt direction may be inconstant, leading to a reduction in the beam coupling efficiency. We have observed that the hybrid cell liquid crystal gain is poor unless care is taken to ensure the Ce:SBN windows are properly poled at the surface. Our preferred poling method involves submerging the crystal and electrode structure in powdered SBN to eliminate (or at least reduce) the dielectric discontinuity which would otherwise exist at the Ce:SBN-air interface. Figure 7 compares the measured gain for one window of Ce:SBN poled in air and poled under powdered SBN. Fitting photorefractive theory [9] to the data for a constant trap density, $N_A = 3.812 \times 10^{15}\,\text{cm}^{-3}$, shows the effective path length for two beam coupling is increased by approximately 60 μm when the crystal is poled under powdered SBN. Although the net change in gain is small, the effective path length increase is most likely due to improved surface poling quality in a 30 μm thick layer close to each surface of the crystal. Windows poled using our powder method were employed for this paper.

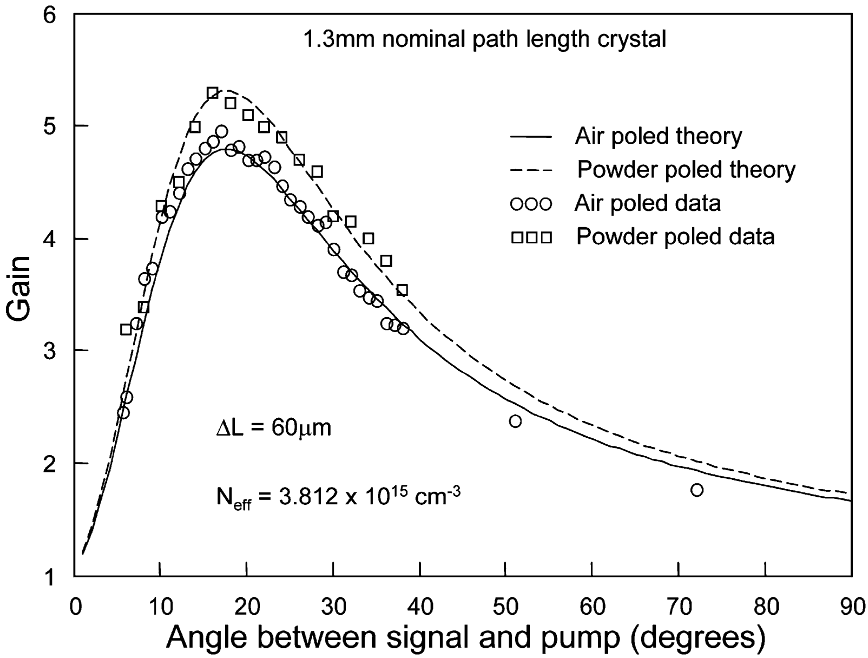

FIGURE 7 Ce:SBN gain characteristics for poling in air and poling under powdered SBN.

CONCLUSIONS

We have demonstrated that the optical gain from liquid crystals in Ce:SBN hybrid cells originates from a combination of surface induced pre-tilt and the flexoelectric effect. We attribute the surface induced pre-tilt effects to the presence of planes of oxygen sites which are inclined with respect to the a-axis in Ce:SBN. The highest gain is achieved with planar aligned cells when the rubbing direction is either parallel or perpendicular to the crystal c-axis. In both cases the gain is sensitive to the rubbing direction. When aligned parallel to the c-axis, the gain is largest when both windows are rubbed towards the negative c-axis. For planar alignment orthogonal to the c-axis, each window has a preferred rubbing direction and the gain is maximized when both windows are rubbed parallel with the same preferred rubbing direction. The dependence of the liquid crystal gain upon the flexoelectric effect leads to increased gain when the cell thickness is reduced. Reliance on surface pre-tilt effects makes it important to ensure that the hybrid cell windows are properly poled at the surfaces.

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