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14. ABSTRACT

This report results from a contract tasking University of Southampton as follows: The main objectives of this exploratory, short project will concern the study of the quality of liquid crystal cells with diluted suspensions of ferroelectric nano-particles and their photorefractive properties. We will use ferroelectric nanoparticles of photorefractive material: thiohypodiphosphate (Sn2P2S6). The actual nano-particles have been produced by a method (fine mechanical grinding), tested earlier. Sn2P2S6 nanoparticles proved, so far, to be the most efficient in enhancing dielectric anisotropy of liquid crystals. As liquid crystal hosts, Merck E7 or ZLI 4801 will be used and cells will be prepared in two configurations. The first configuration will have standard, non-photosensitive aligning layers on both substrates, such as polyimide or low-ionic surfactant. The second configuration will include a photosensitive PVK:C60 layer on one substrate of the cell, instead of polyimide. The LC DSFNP cells with the highest quality will be tested for two-beam coupling gain and the magnitude of diffraction. We will focus our activity on the following targets:

Task	Duration	Timescale
1 Preparing LC DSFNP liquid crystal cells with and without photosensitive polymer layers	4 weeks	4 weeks
2 Inspection and checking the quality of cells	2 weeks	6 weeks
3 Measurement of two-beam coupling gain and diffraction in LC DSFNP cells	4 weeks	10 weeks
4 Analysis of results; final report and conclusions	4 weeks	14 weeks

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FINAL REPORT

Award number: FA8655-05-1-3033

Nanoparticles doped, photorefractive liquid crystals

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3 September 2005

Aims of the project	1
Diluted suspensions of ferroelectric nano-particles in nematic host	2
Liquid crystal cell designs and experimental set-up	3
Main results	4
Conclusions.....	7
Appendix.....	8

Aims of the project

In this feasibility study of ferroelectric nanoparticles doped liquid crystals we focussed on the following tasks. The first task concerned preparing cells containing liquid crystals with dispersed nanoparticles, with and without photosensitive layers, and on checking their uniform alignment. Furthermore, we investigated their photorefractive properties by measuring the efficiency of energy transfer in two-beam coupling and diffraction. The results measured in cells with ferroelectric particles were then compared with the performance of cells containing just pure liquid crystals. The final task was devoted to the summary and discussion of results.

Diluted suspensions of ferroelectric nano-particles in nematic host

Ferroelectric nanoparticles can be successfully incorporated in liquid crystal hosts¹. When ferroelectric nano-particles are dispersed in nematic liquid crystals, their large dipole and high polarizability can lead to strong interaction with liquid crystal molecules. As a result, they share their macroscopic properties with the host via anchoring and volume interactions². Ferroelectric nanoparticles can have significant effect on dielectric properties of the mixture, but due to their small size do not disturb the uniform alignment of liquid crystals.

Suspensions of ferroelectric nanoparticles in nematic host are usually made at low concentration, so the cells appear similar to those with pure liquid crystals. However, the presence of nanoparticles can be confirmed by viewing the cells under a polarising microscope. The other evidence for their influence comes from the unique properties, such as an enhanced dielectric response and sensitivity of the liquid crystal director to the sign of the electric field.

The concentration of ferroelectric nanoparticles of approximately 1% is optimum. Above 5% particles begin to have a noticeable effect on liquid crystals and can undergo significant sedimentation or aggregation. Concentrations above 0.1% are needed for nanoparticles to act collectively on the elastic liquid crystal matrix. There is also a limit on their size. In order for them to maintain their intrinsic properties, they have to be larger than 10 – 20 nm.

Sub-micron particles can be produced by the process of fine milling of ferroelectric material. Crystalline particles of approximately 1 μm in diameter are ground together with a surfactant for approximately 100 hours in a micro-mill. The particles are then sorted and the finest ones are dispersed in a liquid crystal host, kept at the isotropic phase. A typical surfactant used for this purpose is oleic acid. Liquid crystal and nanoparticles are then mixed ultrasonically.

¹ Y. Reznikov, O. Buchnev et al App. Phys. Lett, **82**, 1917 (2003).

² E. Ouskova, O. Buchnev, V. Reshetnyak V, Liq. Cryst. **30**, 1235 (2003).

In this project we used particles of photorefractive material thiohypodiphosphate $\text{Sn}_2\text{P}_2\text{S}_6$. Their typical shape is that of a needle with size $100 \text{ nm} \times 400 \text{ nm}$.

Liquid crystal cell designs and experimental set-up

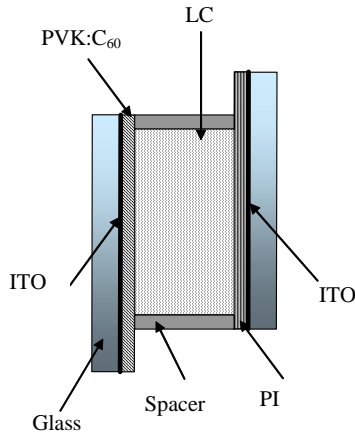


Figure 1 Liquid crystal cell design

The nematic liquid crystals used as hosts were E7 and Merck 18523. The former one has relatively high birefringence ($\Delta n = 0.2$) and is one of the most popular, standard nematic liquid crystals. The latter is more unique as it was specially synthesised to have its refractive index matched to silica. However, it suffers from very low birefringence ($\Delta n = 0.04$). So far it proved impossible to synthesise similar, silica compatible, liquid crystals with higher birefringence.

The cell design was, so called "combined", with one substrate was covered by rubbed polyimide and the other one covered by rubbed layer of photoconductive polymer, polyvinyl carbazole doped with fullerene (PVK:C60). Figure 1 presents a schematic design of such a cell. Its further details are described in the Appendix.

The dynamic holograms and beam coupling effect were induced by two, coherent beams from a frequency doubled CW Nd:YAG laser. The transmitted and first order diffracted beams were measured. We have measured the two-beam coupling gain G defined as: $G = I_{12}/I_1$, where I_1 is the intensity of the probe beam in the absence of the pump beam I_2 and I_{12} is the intensity of the probe beam in the presence of the pump beam.

In order to compare the performance of different cell we calculated use the gain coefficient, Γ , from the experimental data. Γ is defined as: $\Gamma = 1/d' * \ln \frac{Gm}{m-G-1}$ where d' is the effective thickness of the liquid crystal, m is the incident beams intensity ratio. The dependence of gain coefficient on applied DC field was then investigated. As stated earlier, the experiments were carried out both for the ferroelectric nanoparticles suspensions in LC 18523 and in E7 as well as in cells with pure nematic hosts. In the Appendix, the detailed description of the experimental set-up and the procedure is enclosed.

Main results

1. The diluted ferroelectric suspensions of submicron particles of $\text{Sn}_2\text{P}_2\text{S}_6$ were *successfully dispersed* in two nematic hosts – LC 18523 and E7 from Merck.
2. Combined cells, filled with nanoparticles-liquid crystal suspension, were of *high quality*, with both substrates in each cell providing uniform, planar alignment of the suspensions. The cells were then checked in more detail. Figure 2 presents a typical example of uniform alignment observed under illuminating a cell placed under a polarising microscope. Using a microscope objective x 20, cells were inspected and the presence of nanoparticles confirmed. Some clusters of nanoparticles can be seen, so a more detailed analysis using AFM would be necessary to resolve the individual particles.

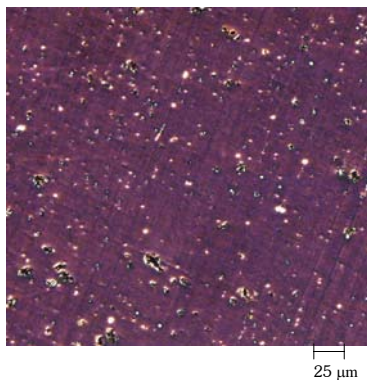


Figure 2
Suspension of ferroelectric nanoparticles in liquid crystal E7 inspected under a polarising microscope

3. Cells with ferroelectric particles appear transparent, as expected, when illuminated by visible light (figure 3).

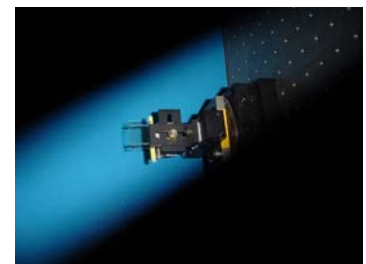


Figure 3
Cell with ferroelectric nanoparticles mounted and illuminated by visible light

4. When a cell with ferroelectric nanoparticles was placed in a two-beam coupling set-up, *energy exchange between the beams was observed*. Figure 4 presents this effect.

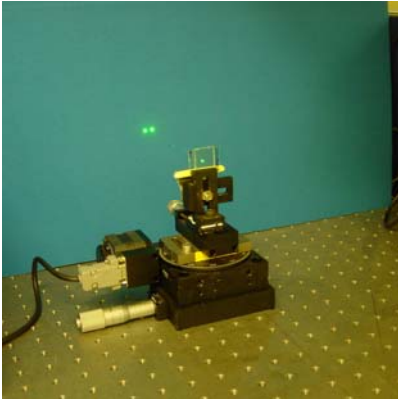


Figure 4
Two-beam coupling in liquid crystal cell doped with ferroelectric nanoparticles

5. The main finding is the evident *enhancement of the photorefractive properties* (gain coefficient) observed *in cells with ferroelectric particles dispersed in LC18523*. The dependence of two-beam coupling gain coefficient on the applied voltage is presented in the Figure 5.

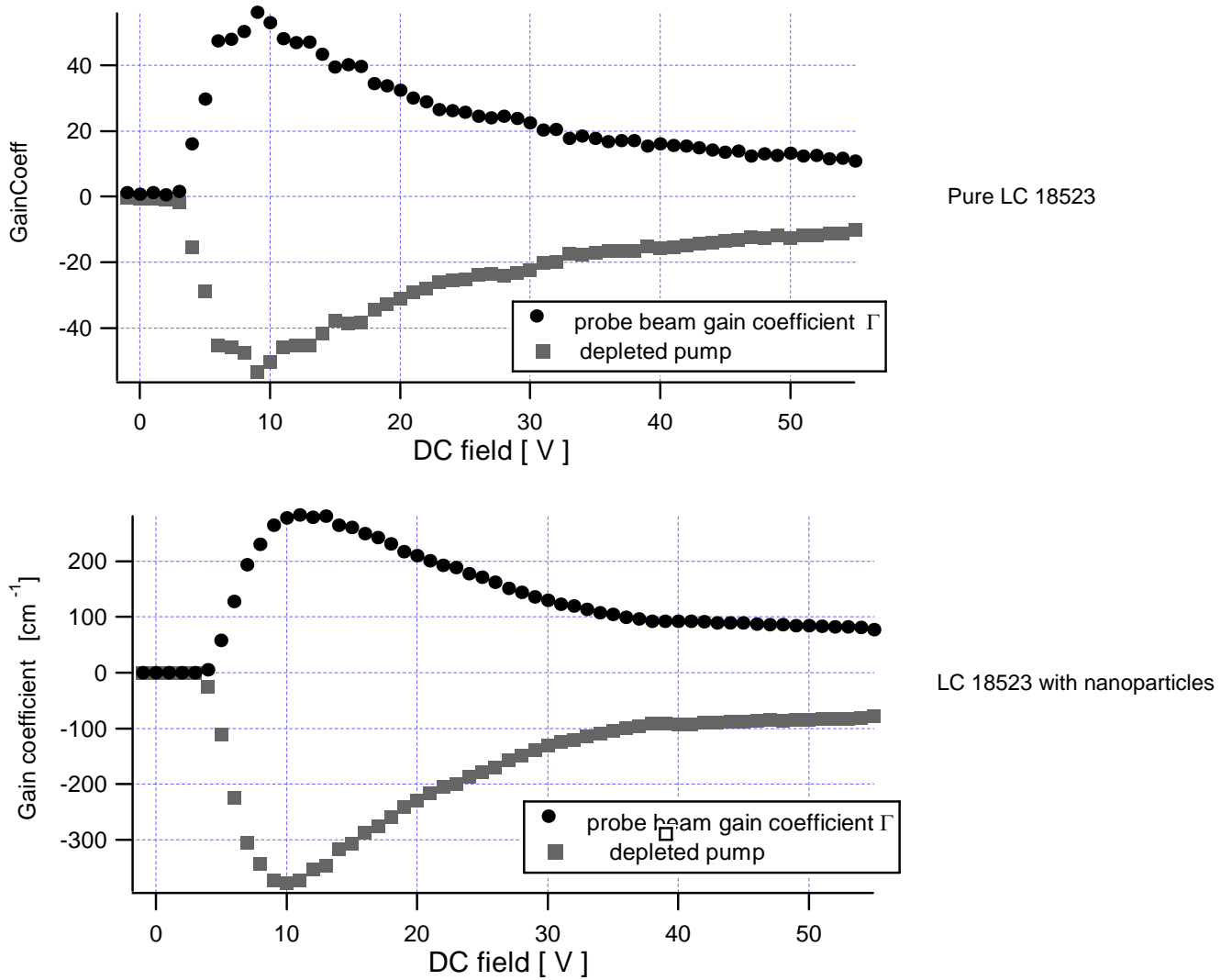


Figure 5 Two-beam coupling gain in pure, undoped liquid crystal Merck 18523 (top) and in ferroelectric nanoparticles suspension in Merck 18523 liquid crystal (bottom)

As expected, both the ferroelectric suspension liquid crystals and pure nematic revealed a strong dependence of the energy transfer between the recording beams on the applied DC-voltage. However, the gain coefficient for the suspension was found to be approximately 5 times higher than for the pure nematic. At the optimum value of the DC- field, $U = 10 \text{ V}$ the gain coefficient in the suspension reached $G_{\text{suspension}} \approx 300$ and for the nematic only $G_{\text{nematic}} \approx 60$.

6. Interestingly, *no significant gain enhancement was observed in ferroelectric suspensions in liquid crystal E7*. Given the relatively high birefringence of this liquid crystal and record high gains already reported, it is likely that the contribution from ferroelectric nanoparticles is not critical for this already efficient and optimised system. Raman-Nath diffraction, an effect that competes with two-beam coupling, was negligible.
7. In addition to the originally proposed tasks, we explored in more detail the effect of nanoparticles on liquid crystal E7. As no significant improvement in two-beam coupling gain was observed by adding ferroelectric nanoparticles, a more straightforward experiment of measuring the transmitted intensity with increasing DC voltage was carried out. The cells were placed between a polariser and an analyser, so

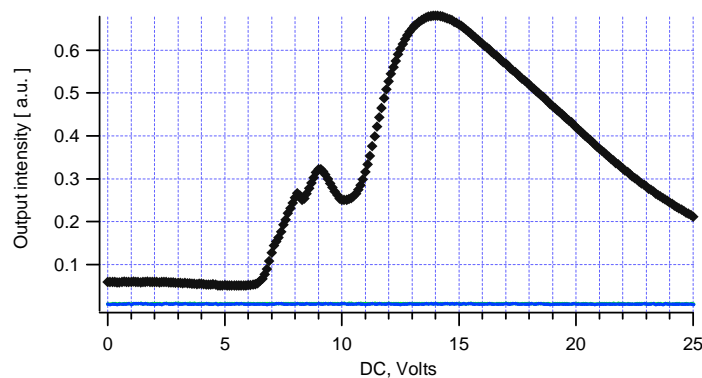
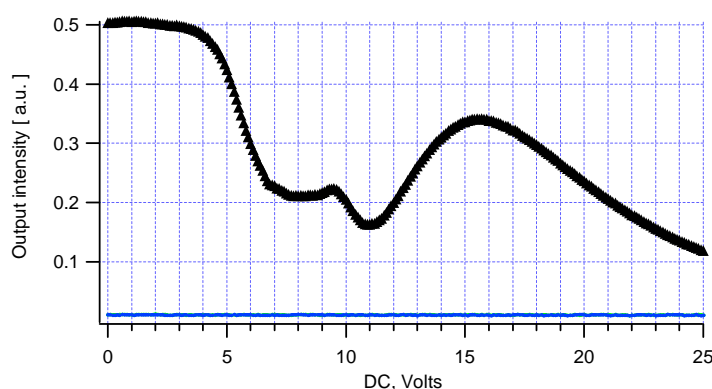


Figure 6
Threshold of reorientation for
pure liquid crystal E7 (a)



liquid crystal E7 with ferroelectric
nanoparticles (b)

any change in liquid crystal alignment would affect transmitted intensity. Depending on the initial position of the two polarisers, the first part of the transmission curve (before the onset of reorientation) is a plateau that is either at maximum or minimum. When the reorientation starts, the transmission curve becomes an increasing (or decreasing) function of applied DC voltage.

The measured transmission versus DC voltage was different in the case of pure nematic than for nanoparticles suspension. Not only the characteristic features were different, but also a *lower threshold of reorientation was observed for samples with ferroelectric nanoparticles*. Figure 6 presents the results of this reorientation threshold for the two cases.

The top graph was taken in a cell with pure E7 liquid crystal and in this case the threshold was higher, namely over 6V. The bottom graph shows the example of a cell with ferroelectric nanoparticles and the threshold of reorientation is approximately 3 V. We can therefore report a *lowering of a threshold by approximately factor of 2 in ferroelectric nanoparticles suspension in liquid crystal E7*.

Conclusions

We successfully completed all experimental tasks outlined in the proposal. Cells with ferroelectric nanoparticles dispersed in two liquid crystals, E7 and Merck 18523 were made. Uniform alignment was achieved as well as two-beam coupling. One of the most exciting and promising results achieved in this project is the two-beam coupling gain enhancement by a factor of 5 in cells with suspension of nanoparticles LC 18523. This indeed, shows the potential of ferroelectric nanoparticles for improving optical response of liquid crystals, especially for those materials where a method of chemical synthesis has reached its limit. Moreover, while for E7 no significant gain enhancement was observed, the threshold of reorientation was reduced by a factor 2 in cells with nanoparticles.

Suspensions of ferroelectric nanoparticles in liquid crystals clearly need to be investigated further to explore in more detail the full potential of those novel hybrid organic-inorganic materials.

Appendix

Measuring two-beam coupling gain and diffraction

Figure 7 presents a schematic diagram of a two-beam coupling experimental set-up, where the intensity of incident and transmitted beams was measured. In our arrangement a liquid crystal cell was mounted on a rotation stage that could be precisely turned around the vertical axis (perpendicular to the plane containing the incident beams) at the point of intersection of the incident beams.

Electric shutters, that blocked or unblocked the beams, as well as application of electric field, were controlled by a computer. The intensity grating, created by the interference of two, horizontally polarized, beams (543 nm) had a spacing of between of 60 μm . This experimental set-up was also used to measure the light and DC field thresholds for reorientation of liquid crystals with single beam illumination. The structure and appearance of an illuminated spot on a sample was simultaneously monitored through second pair of polarisers and backlight and then recorded on a CCD camera. Monitoring of the illuminated area of the cell enabled us to record the dynamics and uniformity of light and electric field driven reorientation.

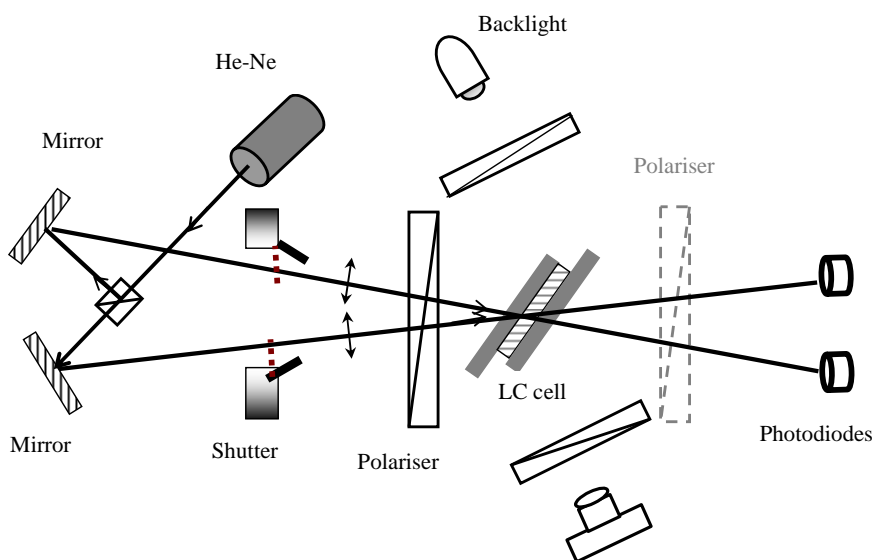


Figure 7

Experimental set-up for measuring diffraction and two-beam coupling

The liquid crystal-polymer cell structure was shown on figure 1. PVK doped with photosensitiser (C_{60}) was deposited as a thin and uniform layer onto ITO covered glass substrates. Both C_{60} and PVK were dissolved in chlorobenzene. Doping of PVK with C_{60} was achieved by adding a saturated

concentration of C₆₀ solution to the PVK solution with concentration of approximately 14.9% by weight. Polymer films were then spincoated onto clean ITO covered glass and dried at high temperature.

The substrates were unidirectionally rubbed and uniform planar alignment was achieved. Doped PVK layer was deposited only on one substrate, while the other was covered with standard polyimide (PI) as an alignment layer. All the cells were 30 μm thick and filled with either liquid crystal or liquid crystal and nanoparticles suspension. A DC bias applied to the cell ITO electrodes had a negative contact applied to the PVK covered substrate.

The experimental procedure for precise detection and measurement of two-beam coupling consisted of several steps where the incident beams were either blocked or unblocked. The value of applied DC field varied from 0 to 56 V. There are several stages of the measurement all controlled by a computer. In step one and two, the shutters were closed and then opened to let both beams through simultaneously. Then, just one beam (pump) was present, followed by a step where both beams were again illuminating a cell. Further, the shutter for the pump beam was closed and for the probe opened. Finally, both beams were let through and then both blocked. In this way, time dependence of beam intensities could be recorded and monitored and the response of the system to transient changes in incident light and applied DC field could be recorded. For measuring the steady-state gain magnitude, the measurements were taken when steady-state values of transmitted intensities were reached and the final, returned value of intensity was taken as an average of 600 data points. This sequence of steps could be repeated for different values of DC field, increasing from zero. The complete experimental procedure allowed us to measure gain and, at the same time, monitor the total change in beam intensities.

Using this experimental methodology, two-beam coupling gain could be measured. The steady-state values of beam intensities were recorded after relaxation of the system to a quasi-equilibrium state.