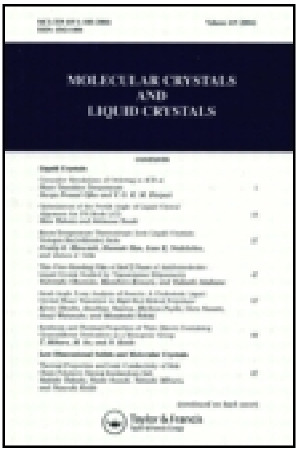

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Second Harmonic Generation Studies of Phase Transitions in Ferroelectric Liquid Crystals

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Second Harmonic Generation Studies of Phase Transitions in Ferroelectric Liquid Crystals

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Phase transitions and switching behaviour in thin (1.5 - 4 μm) planar cells of a ferroelectric liquid crystal (FLC) mixture are studied by optical second harmonic generation (SHG). A pronounced anisotropy of the SHG response shows a high ordering degree of the FLC molecules in the cells. We studied the electric field-induced switching of the FLC cells and their temperature dependence by means of SHG. This shows the existence of a 10-20 nm thick frozen sub-surface layer of FLC molecules,which cannot be switched by an electric field well above the bulk saturating field and at significantly high temperatures.

Keywords: Ferroelectric Liquid Crystals, Second Harmonic Generation, Phase Transition, orientational order of liquid crystals

INTRODUCTION

The first observation of ferroelectricity in liquid crystals goes back to the 1975 paper by Meyer and co-workers [1]. Since then, interest in studies of ferroelectric liquid crystals (FLC) remains permanently high because of their potential applications [2] and interesting fundamental properties as two-dimensional (2D) ferroelectrics. During the last two decades, new nonlinear effects have been observed in FLC using the optical second harmonic generation (SHG) technique. SHG has proved to be a rather simple, non-invasive and informative probe to study the structure, symmetry and morphology of ultrathin films [3]. This advantage of SHG stems from its unique sensitivity to the breakdown of inversion symmetry [4]. The latter results in high sensitivity of the SHG probe to the ferroelectric properties and phase transitions in sub-surface layers and ultrathin films.

In this paper, we studied ferroelectric properties and phase transitions in thin planar FLC cells as well as the switching behaviour using the SHG technique.

EXPERIMENTAL SET-UP

The output of a Q-switched Nd:YAG laser at a wavelength of 1064 nm (pulse intensity of 1-10 MW/cm^2, pulse duration of 15 ns and repetition rate of 12.5 Hz) is used as a fundamental radiation. The cells were mounted on a rotation stage in air and it was arranged in such a way that the smectic layers were horizontally oriented for the azimuthal angle Ψ=0 (when the y-z plane of the laboratory coordinates is parallel to the y'-z' plane of the sample coordinate system, Fig. 1). The temperature of the samples was varied from room temperature to up to 100°C. The fundamental wavelength was filtered out from the SH signal , and viceversa, by using appropriate colour filters. A reference branch, which measured the SH signal generated by a z-cut quartz crystal, was used in order to compensate the intensity fluctuations. The transmission configuration facilitates the identification of the anisotropic tensor components since normal incidence delivers SH signals only from these components. The isotropic components can be gradually introduced by rotating the sample around the x axis. A DC electric field directed along the normal to the cell (z-direction) up to 30 V was applied using the ITO electrodes.

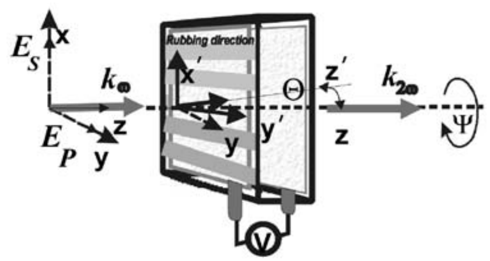

FIGURE 1 Details of the planar aligned FLC cell together with the system of coordinates in transmission. The dark stripes indicate the orientation of the smectic layers. The rubbing direrction was along x'.

MATERIALS AND SAMPLES

Fig. 2 shows the composition of the studied FLC quaternary mixture. It consists of 6.58 wt% (S)-IGS97 in DFT1, which is also a mixture of three components - MH11, MH3 and MH2 (50:25:25 wt%, respectively). The primary dipole moment of the LC molecules is directed perpendicular to the long molecular axes. The SHG measurements are performed in 1.5, 2, 3 and 4 μm thick cells (E.H.C, Tokyo). If the thickness of the cell is much smaller than the bulk helical period of the SmC* phase (12μm for our mixture), unwinding takes place. The interaction forces between the LC molecules and the surface plates are transmitted through the structure by elastic stress, and the result is an unwinding of the helix and homogeneous ordering in the z-direction (perpendicular to the film plane) dictated by the surface [5].

All the cells are equipped with Indium-Tin Oxide (ITO) electrodes and coated with a rubbed polyimide layer for the planar alignment. In this study, we have preferentially used cell configurations with identically brushed polyimide coatings. The rubbing direction is parallel to the x'-axis (Fig. 1). Proper alignment and definition of the bookshelf geometry were obtained by applying a square-wave voltage of alternating polarity (10Hz, 10V), and by a slow cooling of the sample from an isotropic phase to the Sm-C* phase. Without the application of the electric field, we obtained a chevron structure. Two types of phase transitions are expected for this FLC mixture: a SmC*-SmA* transition which takes place at 45°C, and a SmA*-N* at about 95°C.

Reflectivity measurements were also performed in order to estimate the refractive indices of the FLC at the fundamental and SH wavelengths. The corresponding ordinary refractive indices are $n_o(\omega)$ =1.47, $n_o(2\omega)$=1.52 , and the extraordinary are $n_e(\omega)$ = 1.58 and $n_e(2\omega)$ = 1.62.

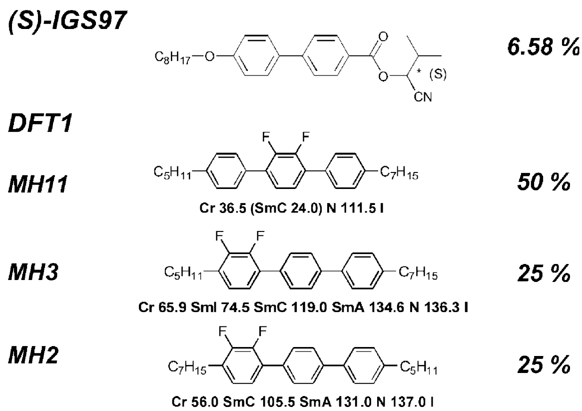

FIGURE 2 Structure of the FLC molecules and their relative weight in the FLC mixture. The phase sequence in the bulk was as follows: Cr (<25°C) SmC* (45.3°C) SmA* (95.4°C) N* (104.9°C) I

EXPERIMENTAL RESULTS.

The SHG experiments were performed for the p-in, s-out or s-in, s-out polarization combinations of the fundamental and SH waves in order to avoid the contribution to the SHG signal coming from the isotropic ITO electrodes [6]. Fig. 3 shows a typical dependence of the p-in, s-out SHG intensity on the azimuthal angle for a 3 μm cell in transmission geometry at nearly normal incidence, at room temperature and without applying an electric field. An anisotropic pattern reveals a four-fold symmetry of the SHG output, which is consistent with the C_2 point group symmetry which applies to FLC [7]. In the experiments described below, the azimuthal orientation of the cells is chosen to correspond to the maximum of the SHG anisotropic dependences.

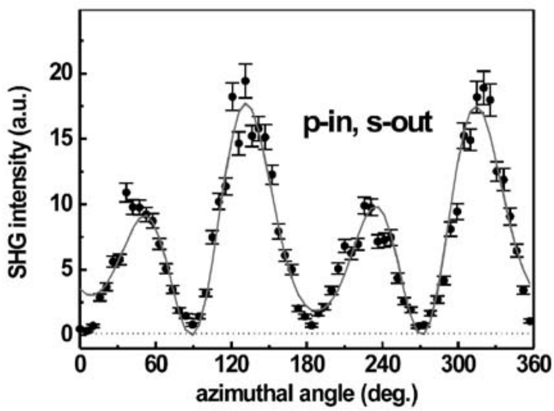

FIGURE 3 SHG azimuthal anisotropy from FLC for the p-in, s-out polarization combination, in transmission geometry (nearly normal incidence) at room temperature without applying electric field.

Fig. 4.a shows the dependence of the SHG intensity on the DC electric field applied to the FLC cell. The experiment is performed in transmission through the FLC cell, which is set at nearly the normal incidence of the fundamental beam, at room temperature. The application of the DC electric field results in a drastic decrease of the SHG intensity for fields of ~ 5 V/μm. The electric field dependence shows typical thresholdless, hysteresis-free switching. Fig. 4.b shows the SH interferograms for the case of +2 V/μm (open circles) and – 2 V/μm (close circles). These interferometry measurements were done by

translating a lambda half plate a distance of 20 cm (see, for instance, ref. [8] for a description of the method). The experiment is performed in the same conditions as in the case of SHG intensity measurements. The SHG interferograms show the same phase for positive and negative fields.

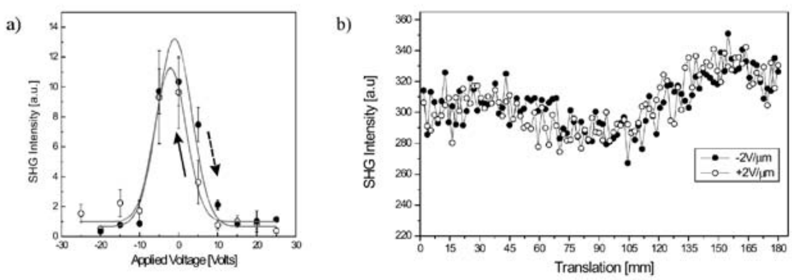

FIGURE 4 a) Dependence of the SHG intensity versus DC electric field applied to the FLC cell; b) SH interferograms for ± 2 V/μm measured in transmission geometry at room temperature for p-s combinations of polarisations.

Fig. 5.a shows the temperature dependences of the SHG intensity for the p-in, s-out polarisation combinations measured in reflection geometry at 45° of incidence. Due to the finite thickness of the cells the phase transitions take place at lower temperatures than in the bulk. A sharp decrease of the SHG intensity is observed in the vicinity of 90°C. This decrease is associated with the transition of the LC to a non polar (N*) phase. The SmC*-SmA* transition, which is

expected at 45°C for the bulk, does not influence drastically the intensity of the SHG response. At the same time, modulations in the SHG intensity are observed for temperatures below 90°C. No hysteresis in the SHG intensity was observed during cooling, and therefore the drastic changes in the SHG intensity in the vicinity of 90°C can be attributed to the SmA*-N* phase transition in FLC. Fig. 5.b shows the temperature dependences of the SHG intensity for the p-in, s-out polarisation combinations measured in transmission geometry at nearly normal incidence. A sharp decrease of the SHG intensity is observed in the vicinity of 40°C, which is associated with the second order SmC*-SmA* phase transition. Both measurements have been done without applying electric field.

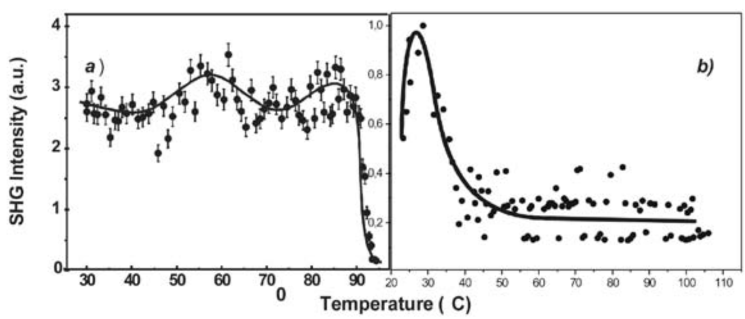

FIGURE 5 Temperature dependence of: a) the SHG intensity in reflection at 45° of incidence and b) in transmission at nearly normal incidence from a 3 μm cell at the maximum of the p-in-s-out azimuthal dependence. Lines are guides for the eyes. No electric field was applied

DISCUSSION

The coherence lengths for the SHG in transmission and in reflection from the cells, $l_{cor} = \pi / (k_{2\omega} \pm 2k_{\omega})$ - where $k_{2\omega}$ and k_{ω} are the wave vectors of the SH and fundamental wavelengths - give the thickness of the layers which participate in SHG in transmission through the cell and in reflection from it. They are about 6 μm and 9 nm respectively, as the corresponding effective refractive indices are $n_{2\omega} = 1.54$ and $n_{\omega} = 1.49$ [9]. This means that about 10-20 layers of LC molecules participate in the SHG process in reflection from the sample, while for the transmission geometry the whole cell takes part in SHG.

The molecules in the studied FLC could be packed in bookshelf and chevron structures. Without applying electric field, bookshelf structures are characterized by a preferential orientation of the molecular directors within each layer and in the neighbouring layers, which results in both the in-plane (directed along the y-axes) and out-of plane (z-component) of the dipole moment (spontaneous polarization P_s). In symmetric chevron structures, the molecular directors of the neighbouring layers are tilted by the same angles with respect to the z-axis so that the in-plane component of the dipole moment of FLC becomes zero, and the film possesses only the z-component of the dipole moment. In our samples an asymmetric chevron is formed due to the subsurface layer tilt in the SmA* phase, so that the chevron cusp is not at the centre of the cell thickness. Nevertheless, in both cases, the FLC structure can reveal the C_2 point group symmetry which is observed experimentally

Applying a DC electric field to FLC cells in both chevron and bookshelf structures results in a reorientation of the molecular dipole moments with respect to the field direction (z-axes) and to the decrease of the in-plane component of the quadratic susceptibility of the film. In our experiments the sample was slightly tilted in comparison with the normal incidence of the fundamental beam. In reflection geometry there are no remarkable changes in the arrangement of the FLC molecules: only few sub-surface layers of FLC molecules placed close to the upper window of the cell are responsible for SHG in reflection geometry. For the transmission geometry the whole cell takes part in SHG. In this geometry the thresholdless switching proceeds via a collective motion of the director field around the surface of the cone with a tilt angle θ, as shown in fig. 6. If the smectic layer is of chevron type, the molecules can choose one half of the azimuthal angle of the cone, since molecules have a tendency to align themselves parallel to a substrate surface, as illustrated in fig. 6 (E=0). The LC molecules rotate toward the opposite directions in the upper and lower halves of the chevron as the in-phase SH signals evidence [10]; in this way, collective molecular switching occurs.

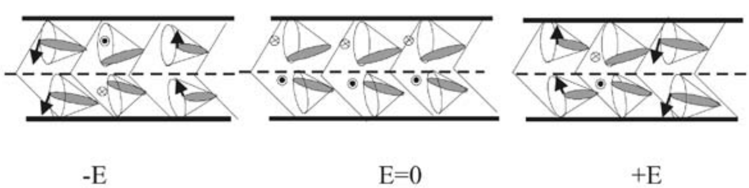

FIGURE 6 Sketch of the collective switching model: the director field proceeds on the surface of the tilt cone.

Finally, we would like to mention the effect of polar surface anchoring. It is well known that polar surface interaction stabilizes a twisted state in which a splay deformation of **P** exists, being **P** the polarization. Then the polarization space charge ρ (- $\nabla \bullet$ **P** [11]) is produced. Hence, molecules tend to form a uniform orientation to avoid the production of polarization charge at E=0. The surface constraint also promotes the uniform alignment [12]. The collective motion of the director field is determined by the coupling of the applied electric field to the Goldstone (phase) mode [11]. Molecules change their orientation continuously due to induced non-zero torque (**P** x **E**) and, as a consequence, a thresholdless switching occurs [13].

The fact that the SHG anisotropy remains the same for the temperatures up to the phase transition at 90°C shows that the symmetry of the upper layers of the FLC structure remains the same up to this critical temperature. The absence of dramatic changes in the temperature dependences of the SHG intensity below 90°C indicates that the structure of the FLC layers doesn't increase to the original D_∞ point group symmetry of the SmA* phase after the sample is heated over 45°C. This is due to the strong stabilizing influence of the cell walls, which induce a small but finite value of the spontaneous polarisation as well as a finite tilt close to the solid interface. The formation of a splayed structure can induce a macroscopic rotation of the smectic layers with respect to the rubbing direction which fixes the molecular direction at the surface [11]. This phenomenon is the so-called surface electroclinic effect [14].

The temperature variations of the FLC structure can be deduced from the temperature dependences of intensity of the SH wave. The decrease of the SHG intensity in the vicinity of 90°C should be attributed to the transformation of the sub-surface layer of the FLC sample into the N* phase.

CONCLUSION

The phase transitions and the switching characteristics under positive and negative DC electric fields are studied by means of SHG measurements. The transition of the sub-surface layers into the N* phase is evident from the sharp decrease of the SHG intensity in the vicinity of 90°C. The absence of dramatic changes in the SHG intensity below this temperature indicates the permanency of the polar order. The switching mechanism is a consequence of the boundary conditions and the resulting surface electroclinic effect.

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