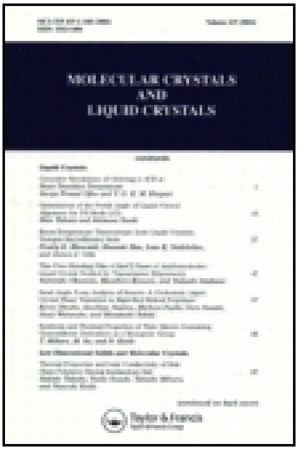

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Byoungchoo Park [b], Moojong Lim [a], Ju-Hyun Lee [a], Jae-Hoon Kim [a] & Sin-Doo Lee [a]

[a] Physics Department, Sogang University, C. P. O. Box 1142, Seoul, Korea

[b] Electronic Materials Research Lab., Institute for Advanced Engineering, C. P. O. Box 2849, Seoul, Korea

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ELECTRIC FIELD-CONTROLLED OPTICAL NONLINEARITY IN FERROELECTRIC LIQUID CRYSTALS

BYOUNGCHOO PARK†, MOOJONG LIM, JU-HYUN LEE,
JAE-HOON KIM and SIN-DOO LEE*
Physics Department, Sogang University, C. P. O. Box 1142, Seoul, Korea
†Electronic Materials Research Lab., Institute for Advanced Engineering,
C. P. O. Box 2849, Seoul, Korea

Abstract We have studied the electric field-controlled optical nonlinearity in a homogeneously aligned ferroelectric liquid crystal (FLC), SCE 13, for understanding the second harmonic generation (SHG) process at a molecular level. From the SHG intensity profiles, measured as a function of the azimuthal angle for rotation at an oblique incidence, all the relevant nonlinear optical (NLO) coefficients are determined self-consistently. It is found that the field dependence of the NLO coefficients can be described in terms of the third-order nonlinearity which couples linearly with a static electric field. The magnitude of the third-order NLO coefficient is of the order of 10^4 pm^2/V^2, which is consistent with the measured value for a racemic version SCE 13R.

INTRODUCTION

Ferroelectric liquid crystals (FLCs) have been extensively studied from the fundamental and application viewpoints.[1] Particularly, FLCs have been recently considered as a potential candidate for use in optical second-harmonic generation (SHG) devices. Based on an elegant physical argument, it was first shown by Meyer *et al.*[2] that the smectic C phase (Sm C*) of the chiral molecules possesses the ferroelectricity. The ferroelectricity arises mainly from a reduced symmetry in the structure of the mesophase caused by the inclusion of a chiral center within the molecular structure of some of the constituent molecules.[2,3]

Owing to the high degree of spontaneous polar ordering, FLCs offer some distinct advantages over other organic systems; self-organization of a non-centrosymmetric structure, optical anisotropy for phase matching,[4,5] and easier processing than crystalline solids. Moreover, a high speed modulation of SHG can be achieved in the FLC devices because of the fast switching of the FLC molecules under an applied electric field. It is, therefore, of great importance to understand the relationship between the polar order at a microscopic level and the electrically controlled macroscopic NLO properties of FLCs.

In the present work, we report on the electric field-controlled optical nonlinearity associated with the polar order present in FLCs. The SHG measurements were carried out as a function of the azimuthal angle for rotation at an oblique incidence (OI) to the surface normal. Using this OI method, we have determined self-consistently the non-centrosymmetric nature of molecular orientation and the resultant NLO coefficients of FLCs. The anomaly observed in the electric field dependence the NLO coefficients is described in terms of a field induced SHG (FISHG) process arising from the third-order optical nonlinearity.

EXPERIMENTAL

The liquid crystal used in this study was a commercially available FLC mixture, SCE 13, from British Drug House. It has the Sm C* phase between −20.0°C and 60.8°C. The molecular tilt ϕ_t and the spontaneous polarization P_s of SCE 13 is 22° and 27.8 nC/cm^2 at 20 °C, respectively. A FLC cell was made up of conductive indium-tin-oxide coated glass substrates, and the cell gap was maintained with glass spacers of 10μm thick. The inner surfaces of the substrates were coated with rubbed polyimide layers, so that the planar, homogeneous alignment of the molecules was promoted.

The SHG measurements were performed using a fundamental beam of a Nd:YAG laser as a light source (repetition rate: 10 Hz, wavelength: 1064 nm, pulse duration: 10 ns, and output power: 10 mJ/pulse). The SHG signal of 532 nm from the cell was monitored with a photomultiplier. All the measurements were performed at the room temperature. The value of d_{11} = 0.49 pm/V for a quartz plate was used as a reference[6] for evaluating the NLO coefficients of the FLC cell being studied.

THE SHG PROPERTIES OF FLC

We first describe the experimental geometry employed for measuring the SHG intensity profiles. The laboratory coordinates are denoted by (1, 2, 3) in Fig. 1. The incident angle θ represents the angle between the surface normal of the FLC cell and the propagation direction of the incident light. The angle ϕ represents the azimuthal angle for rotation with respect to the surface normal.

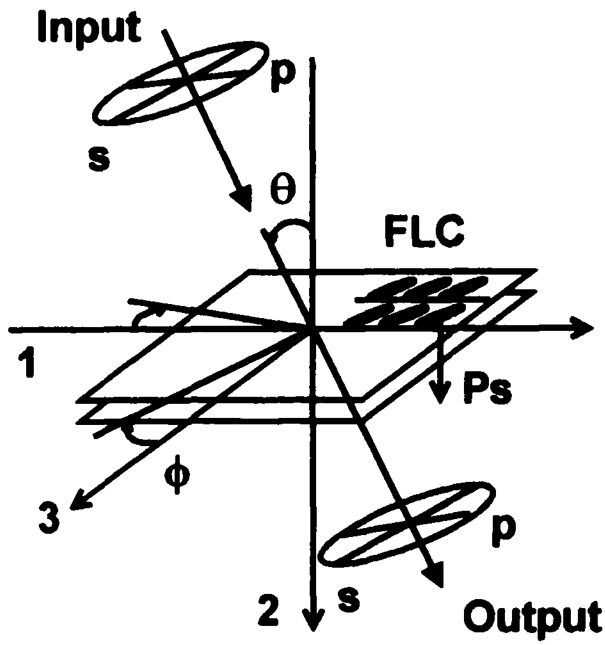

FIGURE 1 (a) The experimental geometry; Input and Output represents the fundamental and SHG beam (p and s are p- and s-polarized). The molecular director of FLC lies in the 1-3 plane.

In the Sm C* phase, the molecular director of the FLC makes an angle ϕ_t with respect to the smectic layer normal and rotates continuously on a cone, moving from one layer to the next, to form a helical structure. In fact, this helical structure is not active to the SHG process. However, in the presence of an applied electric field, it becomes unwound, and the spontaneous polarization P_s tends to orient along the field direction. This unwound state has C_2 symmetry with respect to the polarization direction (axis 2), and then the second-order NLO processes will be involved.

For the fundamental input at the frequency of ω, the output SHG intensity, $I(2\omega)$, from a FLC cell under the electric field is directly proportional to the square of the second-order polarization, $P^2(2\omega)$. When the Kleinman symmetry is properly taken and the biaxiality of the FLC cell is ignored, the expression for each $P(2\omega)$ is written in terms of the input and output polarizations as follows.

$$\begin{aligned}
P_{pp}(2\omega) &= \Big[a_1 d_{14} \sin 2(\phi - \phi_t) + a_2 d_{16} \cos^2(\phi - \phi_t) + a_3 d_{22} \\
&\quad + a_4 d_{23} \sin^2(\phi - \phi_t)\Big] E_p^2(\omega) , \\
P_{ps}(2\omega) &= \Big[2\{a_5 \cos^2(\phi - \phi_t) - a_6 \sin^2(\phi - \phi_t)\} d_{14} \\
&\quad + (a_6 d_{23} - a_5 d_{16}) \sin 2(\phi - \phi_t)\Big] E_p^2(\omega) , \\
P_{sp}(2\omega) &= [-2a_7 d_{14} \sin 2(\phi - \phi_t) + a_7 d_{16} \{1 - \cos 2(\phi - \phi_t)\} \\
&\quad + a_7 d_{23}\{1 + \cos 2(\phi - \phi_t)\}] E_s^2(\omega) , \\
P_{ss}(2\omega) &= 0,
\end{aligned} \tag{1}$$

where

$$\begin{aligned}
a_1 &= 2 \,(\sin\theta_{\omega,o} \cos\theta_{\omega,e} \cos\theta_{2\omega,o} + \cos\theta_{\omega,o} \cos\theta_{\omega,e} \sin\theta_{2\omega,o} \\
&\quad + \sin\theta_{\omega,o} \cos\theta_{\omega,o} \cos\theta_{2\omega,e}) , \\
a_2 &= 2 \,(2\cos\theta_{\omega,o} \sin\theta_{\omega,o} \cos\theta_{2\omega,o} + \cos^2\theta_{\omega,o} \sin\theta_{2\omega,o}) , \\
a_3 &= 2 \,\sin^2\theta_{\omega,o} \sin\theta_{2\omega,o} , \\
a_4 &= 2 \,(\cos^2\theta_{\omega,e} \sin\theta_{2\omega,o} + 2\sin\theta_{\omega,o} \cos\theta_{\omega,e} \cos\theta_{2\omega,e}) , \\
a_5 &= \sin 2\theta_{\omega,o} , \quad a_6 = 2 \,\sin\theta_{\omega,o} \cos\theta_{\omega,e} , \quad a_7 = \sin\theta_{2\omega,o} .
\end{aligned} \tag{2}$$

Note that E's represent the effective components of the fundamental field. In Eq. (1), d_{ij}'s are the relevant second-order NLO coefficients for the C_2 symmetry case. The angle θ_ω in Eq. (2) is given by $\sin^{-1}(\theta/n_\omega)$ with n_ω the refractive index. The subscripts o and e represent the ordinary and extraordinary refractive indices, respectively. The parameters, a_i's, are solely dependent on the refractive indices of the FLC cell and the incident angle θ. In other words, these parameters remain constant for fixed θ. Therefore, one can easily deduce information about the molecular tilt ϕ_t as well as the relevant NLO coefficients of the FLC cell from the ϕ dependence of $I(2\omega)$.

RESULTS AND DISCUSSION

As expected from Eq. (1), the symmetry of the NLO coefficients of the FLC cell are directly reflected by the anisotropy in the SHG profiles as a function the angle ϕ for rotation about the surface normal of the cell. Fig. 2 shows the SHG intensities obtained from SCE 13 for different combinations of polarizations at an applied electric field $E = 10\ V/\mu$m.

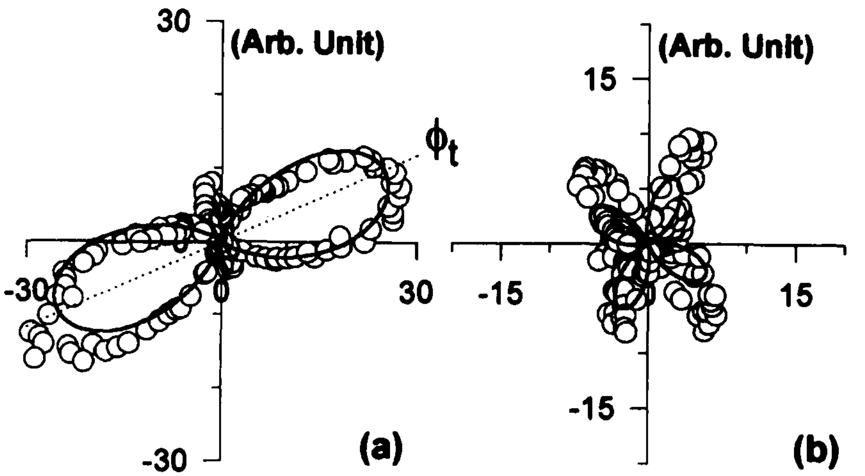

FIGURE 2 The SHG intensities as a function of ϕ for the p-polarized fundamental at $\theta = 50°$; (a) p-polarized and (b) s-polarized SHG. The solid lines represent the least-square fits.

It is clearly seen from Fig. 2 that a substantial anisotropy exists in the SHG profiles, which manifests itself the C_2 symmetry in the Sm C* phase. The solid lines in Fig. 2 are the least-square fits of the data to Eq. (1). From the theoretical fits, the second-order NLO coefficients, d_{ij}'s, and the molecular tilt, ϕ_t, are determined self-consistently. For the case that $E = 10$ V/μm, ϕ_t and d_{ij}'s (in unit of pm/V) are given by $\phi_t = 21.5°$, $d_{22} = 0.337$, $d_{14} = -0.004$, $d_{16} = 0.002$, and $d_{23} = -0.057$. The measured ϕ_t agrees well with the literature value of 22.0°. Moreover, d_{22} and d_{16} are consistent with those obtained from the Maker fringes for the same cell. From the fact that d_{22} is at least one order of the magnitude larger than other NLO coefficients, the polar ordering process of the FLC molecules plays a major role in the magnitude of the spontaneous polarization and the resultant optical nonlinearity.

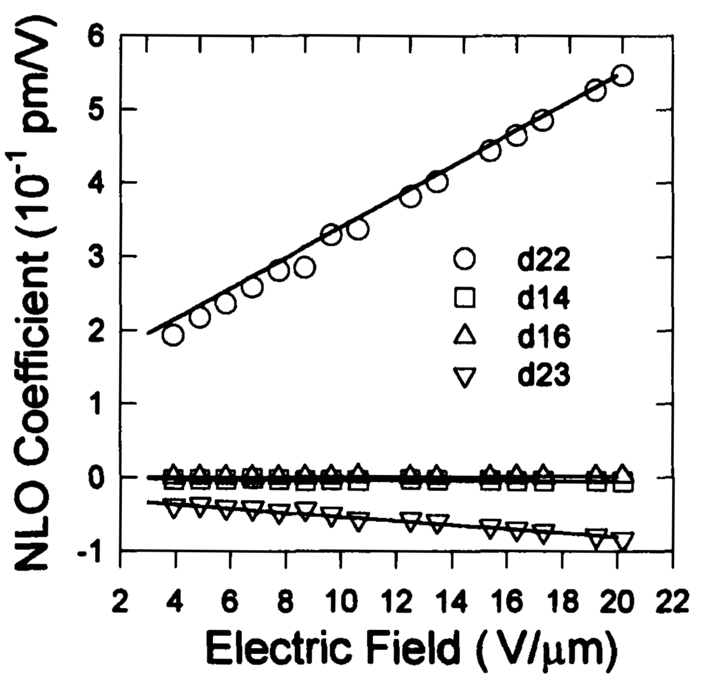

FIGURE 3 The electric field dependence of d_{ij}'s for SCE 13. The sign of each d_{ij} is shown in relative to that of d_{22}. The solid lines are the best linear fits.

One interesting point is that the measured values of d_{ij}'s for our case are somewhat larger than those for other similar FLCs.[7,8] For understanding its physical origin, we looked into the electric field dependence of the NLO coefficients. As shown in Fig. 3, it is clear that d_{ij}'s increase linearly with increasing the electric field above $E = 5$ V/μm. Note that this field is strong enough to unwind the helical structure of the FLC cell. Assuming that the field dependence of $d_{22}(E) = C_0 + C_1\, E(0)$, the best linear fit gives that $C_0 = 0.133$ pm/V and $C_1 = 2.07 \times 10^4$ pm^2/V^2. Since the polar order and orientational one become saturated above $E = 5$ V/μm, this anomaly can not be simply described in terms of the molecular reorientation process. No unusual behavior of the spontaneous polarization, the molecular tilt, and optical birefringence was observed at relatively high fields ($E > 5$ V/μm). This indicates that the anomaly involved in the field dependence of the NLO coefficients may be attributed to the third-order optical nonlinearity of the FLC cell. Specifically, a different type of the second-order processes, i.e., a linear coupling of the third-order nonlinearity with a static electric field $E(0)$, is probably the physical origin. If this is the case, the effective second-order NLO process from the third-order nonlinearity is given by

$$d_{ijk}(E) = \frac{1}{2}\chi^{(2)}_{ijk}(-2\omega, \omega, \omega) + \frac{3}{2}\chi^{(3)}_{ijkl}(-2\omega, \omega, \omega; 0) f_0 E_l(0) \ , \qquad (3)$$

where f_0 is the Onsager local field factor.[9] The field dependence is then described in terms of $\chi^{(3)}_{ijkl}E_l(0)$ term. With the help of Eq. (3), $f_o \approx 1.8$, and the field dependence of d_{22} for SCE 13, $\chi^{(2)}_{22}$ and $\chi^{(3)}_{2222}$ are estimated as 0.26 pm/V and 0.76×10^4 pm^2/V^2, respectively. The magnitude of $\chi^{(3)}_{2222}$ is comparable to that for a typical nematic LC, MBBA[10] ($\sim 0.2 \times 10^4$ pm^2/V^2).

The above argument is further supported by the FISHG results for a racemic version, SCE 13R. The SCE 13R has no polar order at all, and thus no polarization exists in the Sm C phase. The FISHG intensity profiles from SCE 13R are similar to those from SCE 13 except for $\phi_t = 0$. The measured value of $\chi^{(2)}_{22}$ for SCE 13R is essentially zero. However, $\chi^{(3)}_{2222} \sim 1.0 \times 10^4$ pm^2/V^2, which agrees well with that for SCE 13. Again, this tells us that the anomaly in the field dependence of the NLO coefficients comes mainly from the third-order NLO process. Details of the microscopic description of the above argument will be presented elsewhere.

CONCLUDING REMARKS

We have studied the nature of polar ordering and the electrically controlled NLO properties of a homogeneously aligned FLC cell. By employing the OI method, the anisotropy in the NLO coefficients were determined self-consistently from the SHG intensity profiles. The anomaly observed in the field dependence of the NLO coefficients was described in terms of the third-order optical nonlinearity which couples linearly with a static electric field. Further studies on the dynamics of the electric field-controlled NLO properties of FLCs remain to be explored.

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REFERENCES

1. For comprehensive discussion, see Ferroelectric Liquid Crystals, eds., J. W. Goodby *el al.* (Gordon Breach, Philadelphia, 1991).
2. R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris) Lett. 36, L-69 (1975).
3. R. B. Meyer, Mol. Cryst. Liq. Cryst. 40, 30 (1977).
4. K. E. Arnett, S. P. Velsko, and D. M. Walba, Appl. Phys. Lett. 64, 2919 (1994).
5. K. Yoshino, M. Utsumi, Y. Morita, Y. Sadohara, and M. Ozaki, Liq. Cryst., 14, 1021 (1993).
6. J. Jerphagnon and S. Kurtz, S. Phys. Rev. B 1, 1739 (1970).
7. L. M. Blinov and L. A. Beresnev, Sov. Phys. Usp. 27, 492 (1984).
8. J. Y. Liu, M. G. Robinson, K. M. Johnson, and D. Doroski, Opt. Lett. 15, 267 (1990).
9. P. N. Prasad and D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers (Wiley, New York, 1991), p. 65.
10. K. Y. Wong and A. F. Garito, Phys. Rev. A 34, 5051 (1986).