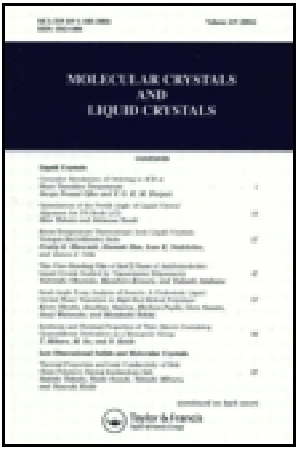

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Flexoelectric Induced Second-Harmonic Generation in a Nematic Liquid Crystal

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Optical second-harmonic generation has been observed in nematic thin films prepared by rubbing technique. The observed second-harmonic is shown to be due to flexoelectric effect. Our results reaffirm that nematic phase possesses overall centrosymmetry.

I INTRODUCTION

Liquid crystals exhibit many interesting third-order nonlinear optical effects.[1] Unusually large optical Kerr effect[2,3] and strong self-focusing[4] have been observed near the isotropic to nematic phase transition. Phase-matched third harmonic generation[5] and d.c.-field-induced second harmonic generation[6,7] have also been observed in cholesteric (CLC) and nematic (NLC) liquid crystals. However, second-order nonlinear processes are not expected to occur in NLC and CLC because these two phases possess overall inversion symmetry[8], i.e., the physical equivalence of the director direction $\hat{n}$ and $-\hat{n}$. In fact, the absence or presence of optical second-harmonic generation (SHG) provides a reliable determination of the presence or absence of centrosymmetry in crystal structures.[9] The method is especially useful when X-ray results do not provide unambiguous conclusions. Earlier experiments[10,11] on CLC and NLC indicate SHG is indeed absent in these two phases, providing strong support that $\hat{n}$ and $-\hat{n}$ are physically equivalent in CLC and NLC. However, Arakelyan et al.[12] recently reported that they had observed SHG in

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well aligned samples of nematic liquid crystal MBBA (p-methoxy benzylidene p-n-butylanilane). These authors, therefore, questioned the generally accepted view that $\hat{n}$ and $-\hat{n}$ are physically indistinguishable in NLC and CLC. In view of the fundamental importance of this question, we have performed SHG experiments on aligned samples of NLC MBBA. Our results show that SHG can be observed only in samples with distortion in its director field. No SHG is present in samples which exhibit sharp conoscopic figures. Analysis based on our experimental results indicates that flexoelectric effect is responsible for the observed SHG. Our results reaffirm that NLC and CLC possess overall centrosymmetry.

II EXPERIMENT

A Q-switched Nd-Yag laser operating at 1.06μm and a repetition rate of 10pps was used to provide the fundamental beam. The laser pulses had a pulse width of 15ns. There was a polarization rotator between the laser and the sample cell so that the polarization of the fundamental beam can be adjusted to any desired orientation. The beam was weakly focused with a 100cm lens so that the beam size on the sample was about 0.3mm. The maximum laser intensity used was kept below the damaging threshold which was $\sim 10^9 W/cm^2$. Second-harmonic signal was detected with a high gain (10^7) photomultiplier (RCA 8575). The output of the photomultiplier was measured with a gated integrator using a gate width of 10μs and an integration time constant of 5 seconds. An interference filter, a $CuSO_4$ cell and a dichroic filter were used to prevent the fundamental beam from reaching the photomultiplier. The overall sensitivity of our system allowed us to measure signal as low as 30 second-harmonic photons per shot with an accuracy of $\pm 10\%$. This sensitivity is sufficient for reliable detection of the presence or absence of SHG in liquid crystals even with fundamental beam intensity well below the damaging threshold. In fact, the same system was found to be more than adequate for measuring third order nonlinear optical processes in NLC.[6,7]

The MBBA used in our experiments was purchased from Atomergic Chemicals Corp. and was used without further purification. The nematic to isotropic transition (N-I) temperature of freshly prepared thin film samples was 43°C. In our experiment, we used only homogeneously aligned samples. The alignment was achieved either by unidirectional rubbing of carefully cleaned microscopic slides or by using fused quartz plates coated with SiO evaporated obliquely onto the plates.[13] The quality of the alignment was checked by monitoring the conoscopic figure obtained with a focused He-Ne laser beam.[14] Distortion in the director field over areas as small as 20μm across could be readily detected. The thickness of samples used in the experiments ranged from a few tens to about 200 microns.

III RESULTS AND DISCUSSION

In samples with satisfactory alignment as evidenced by the presence of clear conoscopic figure of families of hyperbolae like fringes in these samples, no SHG was detected. However, strong SHG was observed in samples with distortion in the director field. These samples did not show clear conoscopic figure and they were prepared by rubbing with unidirectional "hard" strokes. Additional information about the director distortion was obtained from the following observation. When an unfocused He-Ne laser beam linearly polarized along the rubbing direction was sent through these thin film samples, the beam was scattered into a streak perpendicular to the rubbing direction. However, for He-Ne laser beam linearly polarized perpendicular to the rubbing direction, virtually no scattering was observed. These observations indicate that the director of these samples prepared by rubbing with "hard" strokes tilts away from the substrate surface with the director lying in the plane formed by the rubbing direction and the normal of the substrate surface. The degree of tilting, however, varies randomly across the substrate surface making the thin film sample appear as a random grating for light polarized parallel to the rubbing direction.

The SHG observed in these samples was strongly polarized perpendicular to the rubbing direction with extinction ratio ≥ 10. For a linearly polarized fundamental beam, the observed SHG intensity $I^{2\omega}$ varied as a function of θ, the angle between the polarization direction of the fundamental beam and the rubbing direction. As shown in Figure 1, the angular variation closely followed a $\sin^2 2\theta$ dependence. This indicates the dominant contribution to the SHG is due to an effective nonlinear susceptibility χ^{eff}_{xxz}, where we have taken z to be along the rubbing direction, x to be in the plane of the substrate surface, and y to be the beam propagation direction which is normal to the substrate surface. For a linearly polarized fundamental beam, this nonlinear susceptibility leads to a nonlinear polarization $P^{2\omega}_x \propto \chi^{eff}_{xxz} E^{\omega}_x E^{\omega}_z = \chi^{eff}_{xxz} |E^{\omega}|^2 \sin\theta\cos\theta$ and hence the observed θ dependence of I^2_x since $I^{2\omega}_x \propto P^2_x \propto \sin^2 2\theta$. The temperature dependence of $I^{2\omega}_x$ is shown in Figure 2. In the nematic phase, the SHG intensity decreased slightly with increasing temperature but dropped rapidly to zero at the N-I transition temperature. We had also measured the sample length dependence of the SHG intensity. Within $\pm 10\%$, the SHG intensity was independent of sample thickness and did not exhibit any clear coherence length effect. This indicates that the observed SHG is generated in a region whose thickness is thinner than or comparable to a coherence length which is a few microns for MBBA.

From the above observations, it is clear that the observed SHG is due to flexoelectric effect. Rubbing with "hard" strokes produces aligned sample with distortion in its director field near the substrate surface. This distortion leads to a linear polarization that destroys the overall centrosymmetry of

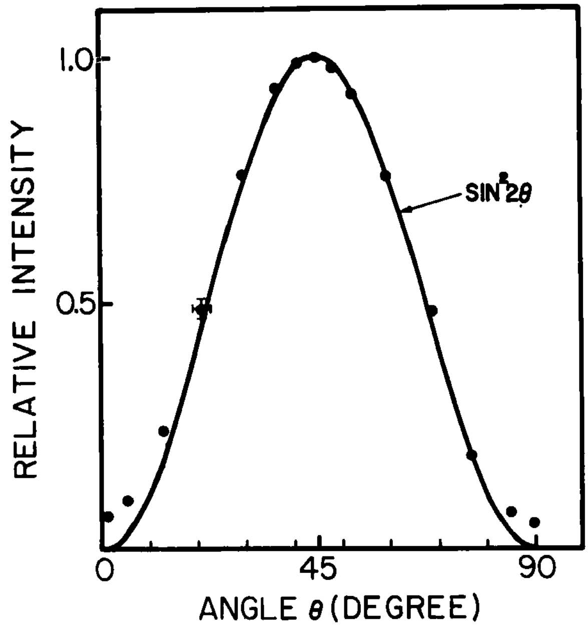

FIGURE 1 Second-harmonic intensity in MBBA as a function of the angle θ.

nematic phase and hence gives rise to SHG. From the polarization dependence of the scattering of He-Ne laser beam, we know the director field near the substrate surface is of the form

$$n_z = \cos\phi(x,y)$$
$$n_y = \sin\phi(x,y)$$
$$n_x = 0$$

While the exact form of $\phi(x,y)$ may be complicated, it suffices for a qualitative analysis to assume that

$$\phi(x,y) = A \sin kx\, e^{-\alpha y} \quad (2)$$

with $A \ll 1$. Due to the flexoelectric effect, this director field leads to a linear polarization given by[8]

$$P^d = e_1 \hat{n}(\nabla \cdot \hat{n}) + e_3(\nabla \times \hat{n}) \times \hat{n} \quad (3)$$

where e_1 and e_3 are the flexoelectric coefficients. To first order in A, we obtain from Eqs. (1), (2) and (3) a linear polarization

$$P_2^d = -e_1\, \alpha\, A \sin kx\, e^{-\alpha y} \quad (4)$$

The nematic medium then becomes effectively a uniaxial system without

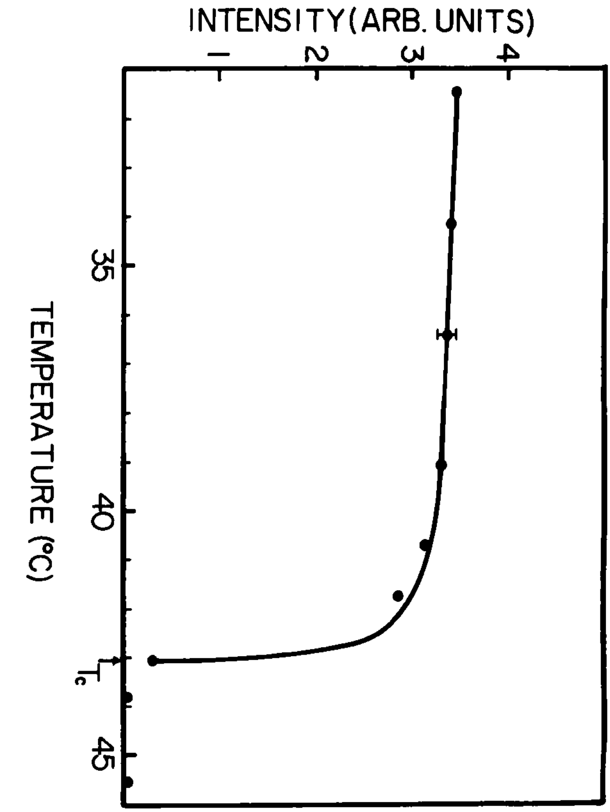

FIGURE 2 Temperature dependence of second-harmonic generation in MBBA.

centrosymmetry. From symmetry consideration,[15] the only nonvanishing second-order nonlinear susceptibilities for this medium are $\chi^{eff}_{xxz} = \chi^{eff}_{yyz} = \chi^{eff}_{zxx} = \chi^{eff}_{zyy}$ and χ^{eff}_{zzz}. The fact that we only observed significant SHG from χ^{eff}_{xxz} is probably due to the following two reasons. First, the SHG due to χ^{eff}_{zzz} and χ^{eff}_{zxx} would be polarized along the rubbing direction and hence would be scattered by the random grating effect of the director distortion. A large part of the SHG signal would have missed the photomultiplier. Second, using the refractive indices of MBBA at 5320A° and 1.064μm[16], we calculated the SHG coherent length to be 0.8μm for χ^{eff}_{zxx} geometry, 2.2μm for χ^{eff}_{zzz}, and 7.2 m for χ^{eff}_{xxz}. Thus, if $1/\alpha$ is $\lesssim 7.2\mu$m but $\gg 2.2\mu$m, the SHG generated will be dominantly due to χ^{eff}_{xxz} as was observed in our experiments.

IV. CONCLUSION

We have observed SHG from MBBA thin film samples which have distortion in their director field. We have shown that our experimental results can be explained well by the flexoelectric effect and the observed SHG in NLC MBBA is not due to the lack of centrosymmetry in the nematic phase. We notice that Arakelyan et al.[12] used in their experiment NLC samples prepared by rubbing technique and they did not check the quality of alignment by monitoring the conoscopic figures. We, therefore, believe the SHG observed in their experiment is also due to flexoelectric effect and not due to the lack of centrosymmetry in NLC.

Acknowledgments

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