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Citation: [Journal of Applied Physics](#) **119**, 124103 (2016); doi: 10.1063/1.4944607

View online: <http://dx.doi.org/10.1063/1.4944607>

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Wide range room temperature electroclinic liquid crystal mixture with large induced tilt and very small layer contraction

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(Received 22 November 2015; accepted 8 March 2016; published online 22 March 2016)

Optical polarizing microscopy, synchrotron X-ray scattering, and electro-optic studies in the SmA* phase of a formulated wide range room temperature liquid crystal mixture indicate a large electric field induced optical tilt up to 23.5° along with a very small contraction of smectic layers. Applied field primarily lifts the zero-field degeneracy of the azimuthal order of the molecules in smectic layers resulting in small layer contraction. © 2016 AIP Publishing LLC.
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I. INTRODUCTION

Chiral smectic-A (SmA*) liquid crystal that exhibits field induced tilts has potentials for applications in fast, gray-scale display devices, micro-colour filters, tunable colour filters, switches, and optically addressed spatial light modulators.^{1–7} The induction of tilt in SmA* phase arising from the coupling of transverse dipole moment of chiral molecule to an applied electric field is known as electroclinic effect (ECE) and was first observed by Garoff and Meyer.^{8,9} The ECE was described by a phenomenological model derived from the Landau theory which predicts a linear dependence of the induced tilt angle at low applied field;⁷ linearity deviates at high field and near orthogonal SmA* phase to the tilted SmC* phase transition temperature.^{10,11} At a given amplitude of electric field, induced tilt is higher near SmC* to SmA* phase transition and the compounds, which have high values of spontaneous polarization in SmC* phase, show a large electroclinic effect due to the induced polarization in SmA* phase. However, in most of the electro-clinic materials, induced tilt is accompanied by a corresponding layer contraction which results in a buckling of the layers.^{12,13} Buckling of the layers is easily observed in an optical microscope as periodic stripes¹⁴ and reduces the contrast ratio high value of which is necessary for display applications. To solve this problem, numbers of groups have investigated the ECE of liquid crystals with “de Vries-like”¹⁵ properties which exhibit very small layer contractions¹⁶ with high induced optical tilt angles.^{17–19} Temperature range of the SmA* phase is also important, because most of the electro-clinic liquid crystals form ferroelectric SmC* phase on cooling or crystallize at room temperature which is detrimental for practical application.

In this article, we report detailed results of optical microscopy, electro-optic, and synchrotron diffraction studies on a wide range room temperature SmA* liquid crystal mixture focusing on its electro-clinic behaviour. Field induced optical tilt as large as $\sim 23.5^\circ$ with less than 0.1% contraction of the layers was observed.

II. EXPERIMENTAL

For the preparation of the mixture, a multi-component matrix was used as host and a chiral compound as dopant.

For creating base matrix, we used four achiral phenyl pyrimidine compounds having tilted SmC phase. Molecular structures and composition of the mixing components are presented in Fig. 1.

A fluorinated chiral compound exhibiting high spontaneous polarisation (~ 230 nC/cm²) with chiral centre at one end was used as dopant. Molecular structure of the dopant and composition of the final mixture are shown in Fig. 2. Higher dopant concentration mixtures show very broad range room temperature ferroelectric SmC* phase,²⁰ not suitable for the ECE based applications.

Polyimide-coated homogeneous (HG) dielectric cell, made of low resistive (about $20 \Omega/\text{cm}^2$) transparent indium tin oxide (ITO) electrodes having an effective area of 1 cm^2 and a cell gap of $\sim 5 \mu\text{m}$, was used. Cell was filled by capillary action with samples in isotropic state. Very slow regulated cooling of the sample was made to get proper alignment.²¹ This cell was used for optical polarizing microscopy, electro-optic, and synchrotron diffraction study. Phase behaviour and transition temperatures of the mixture were investigated by studying its topological defect structures under an Olympus BX41 polarizing microscope equipped with a CCD camera; temperature regulation was made, within $\pm 0.1^\circ\text{C}$, using a Mettler FP82 central processor and FP84 hot stage.

Since in an ac field the chiral molecules switch around an imaginary cone through twice the tilt angle thereby reversing the sign of the spontaneous polarization, tilt of the molecules in smectic layers (θ_{opt}) was determined by measuring the angle of rotation of the FLC cell between two extinction conditions while observing, under polarizing

FIG. 1. Molecular structures of the host matrix: (a) H1 ($n=9$, $m=9$); (b) H2 ($n=9$, $m=7$); (c) H3 ($n=7$, $m=9$); (d) H4 ($n=8$, $m=6$); composition: H1 + H2 + H3 + H4: 20% + 20% + 20% + 40%; transition temperatures: Cr 18°C SmC 69.4°C SmA 78.7°C N 81.2°C Iso.

FIG. 2. Molecular structure of the dopant. Mixture composition: Host + Dopant: 90% + 10%; Transition temperatures: 17 °C < SmA* 63 °C Iso.

microscope, switching of the molecules subjected to (5 Vpp–70 Vpp, 10 mHz) square wave pulses.²²

Tilt was also measured by diffraction study using synchrotron X-ray radiation (PETRA III beam line at P07 Physics Hutch station, DESY, Hamburg) to avoid absorption by glass plates of the cell; the beam was made to incident at the interface but parallel to the cell surfaces, as shown in Fig. 3. The mixture was taken in the dielectric cell and very slowly cooled down from isotropic phase to the desired temperature to get it aligned. 10 images of exposure time 0.1 s were grabbed and averaged to get one diffraction image, and three such images were collected at a particular temperature, with and without electric field. All the physical parameters were averaged over these three image data. A Perkin Elmer 2D detector of pixel size $200 \times 200 \mu\text{m}$ and total size $400 \times 400 \text{ mm}$ was used for image grabbing which was placed 3.3 m away from the sample. QXRD program for PE Area Detectors (G Jennings, version 0.9.8, 64 bit) was used for data acquisition and also for analyzing the images. Images were integrated using a step size of 0.001 to get intensity versus wave vector (Q) distribution. Induced X-ray tilt was determined by using the relation $\theta_{\text{x-ray}} = \cos^{-1} \frac{d(E)}{d}$, where $d(E)$ and d are the layer spacings with and without application of electric field, respectively, assuming a model of hard spherocylinders in which the layer contraction scales with the cosine of the tilt angle. The “de Vries-like” character of the smectic liquid crystal, quantified on a scale of 0 (perfect “de Vries”) to 1 (conventional SmA*–SmC* transition) at a temperature T by the reduction factor R , was determined according to the equation:¹⁷ $R = \theta_{\text{x-ray}}/\theta_{\text{opt}}$.

FIG. 3. Schematic diagram of synchrotron X-ray diffraction set up with dielectric cell parameters (not to scale).

Layers shrinkage was calculated using the relation $\frac{d-d(E)}{d} \times 100\%$.

Response time was determined by measuring the time delay of occurrence of polarization bump from the applied square pulse edge (4–25 Vpp, 10 Hz) while monitoring, in a storage oscilloscope (Tektronix TDS 2012B), the voltage across a resistor in series with the cell.^{23,24}

III. RESULTS AND DISCUSSION

The mixture shows SmA* phase from 63 °C down to 17 °C (below which we could not cool) thus satisfying the basic material need intended for display applications. Textures obtained by applying a 10 Hz square ac field at voltages $5 \text{ V}/\mu\text{m}$ and $15 \text{ V}/\mu\text{m}$ are shown in Fig. 4, in which almost no optical stripe pattern generated by the ECE is visible which may be ascribed to a minimum contraction of smectic layers during electroclinic switching thus solving the contrast ratio problem.

Variation of $\theta_{\text{x-ray}}$ and θ_{opt} with applied electric field at some selected temperatures are shown in Fig. 5. At low temperatures, both $\theta_{\text{x-ray}}$ and θ_{opt} show linear behaviour only at

FIG. 4. Polarized photomicrographs at 25 °C (a) $5 \text{ V}/\mu\text{m}$ and (b) $15 \text{ V}/\mu\text{m}$.

FIG. 5. Variation of induced tilts with electric field at selected temperatures: (a) $\theta_{\text{X-ray}}$ and (b) θ_{opt} .

low electric field and appear to saturate at high field. But, at high temperatures we find the expected linear increase in the induced tilts with applied field.⁸ At a particular field, both tilts decrease with temperature. We further note that the two tilts qualitatively show similar temperature and field dependence, but X-ray tilt is much smaller than optical tilt. To generate gray scale display between crossed polarisers, however, linear dependence of optical tilt on electric field is utilized. In SmA* phase of a pure organosiloxane compound, Spector *et al.*²⁵ also reported that X-ray tilt is much smaller than optical tilt. X-ray tilt is a result of tilt of electron density function of the whole molecule whereas optical tilt arises due to tilt of only the rigid polarisable group of the molecule. Since the host and the dopant molecules possess large flexible parts, X-ray tilt may be much less than the optical tilt. Bartolino *et al.*²⁶ explained the disagreement by considering the “zig-zag” configuration of the liquid crystal molecules having long flexible chains. The zig-zag is composed of an aromatic rigid core that tilts with the layer plane somewhat independently of the flexible end chains which contact the layer planes with temperature independent angle.

To probe further the origin of tilt, layer spacings were measured from synchrotron diffraction study at different temperatures with (15 V/μm) and without electric field and are shown in Fig. 6(a). From ambient as we increase the temperature layers spacing increases up to 28 °C and then

FIG. 6. Variation of (a) layer spacing and (b) relative layer spacing with temperature and (c) variation of layer spacing and layer shrinkage with electric field.

decreases till 45 °C, above which no change in the layer spacing was observed with applied electric field. This increase of layer spacings upon cooling up to 28 °C signifies that the layer expansivity is negative. This behaviour is probably a consequence of increased effective molecular length due to the extension of flexible molecular tails at lower temperature and has previously been observed in fluorinated liquid crystals.^{17,27}

The profile of the relative layer spacing $d(E)/d$ with temperature is shown in Fig. 6(b), and electric field dependence of layer spacing and layer shrinkage is shown in Fig. 6(c). Almost no layer contraction is observed with field which suggests that the mixture is “de Vries-like.” Maximum layer contraction was observed at ~25 °C. At this temperature, zero field layers spacing was found to be 31.643 Å that contracted to 31.618 Å giving rise to maximum layer shrinkage

FIG. 7. Variation of response time with electric field at 20 °C (Inset, temperature variation of response time at 2 V/μm).

of 0.08% and reduction factor R of 0.11. Thus, the present mixture is one of the best “de Vries-like” liquid crystal mixtures that counteracts the layer contraction caused by tilting to such an extent that the layer spacing is restored on application of electric field. Large induced tilt accompanied by very small layer shrinkage is primarily due to development of azimuthal orientational order in molecule which is already tilted in a cone in the absence of the electric field.²⁸ Change of molecular conformation with field and segmented tilt of different magnitudes of the rigid core and flexible tails of the molecules might also contribute to the above result. By extrapolation to zero voltage azimuthally degenerate polar tilt of the mixture was found to be $\sim 5^\circ$ at 25 °C.

To explore further the suitability of the mixture, response time (τ) was determined as a function of applied field at 20 °C, also its temperature dependence at a fixed field (2 V/μm); results are shown in Fig. 7. Thus the mixture shows microsecond order switching which decreases with driving voltage and temperature. Response time at 20 °C is about 25 μs at 5 V driving voltage for a 1.2 μm cell.

IV. CONCLUSION

In summary, we have formulated a room temperature “de Vries-like” SmA* liquid crystal mixture which exhibits large field induced optical tilt ($\sim 23^\circ$) with less than 0.1% shrinkage of layers which were confirmed by texture and synchrotron diffraction study. The mixture will thus be suitable for developing electroclinic devices free from defects due to buckling of layers.

ACKNOWLEDGMENTS

We are thankful to DST, India for providing financial assistance to perform experiments at DESY, Germany. We are also grateful to Professor R. Dabrowski, Military University of Technology, Poland for supplying the compounds. Technical assistance during the experiment provided by Uta Ruet, Olof Gutowski, and Abhishak Sharma, DESY Photon Science Centre is sincerely acknowledged.

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