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Electro-Optic and Dielectric Properties of an Antiferroelectric Liquid Crystal Material

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Results reported in this paper on the electro-optic properties and dielectric relaxation in the SmC_A^* and SmC^* phase of a liquid material as a function of sample thickness. The measurements were carried out in $3\mu\text{m}$, $6\mu\text{m}$, and $10\mu\text{m}$ thick cells. In the whole SmC^* phase two modes were obtained in the low frequency region of the dielectric spectra in each of the three cells without bias electric field. The relaxation strength of both the modes sharply decreases with the applied bias dc electric field. One of the modes is assigned as Goldstone mode, arises due to phase fluctuation and the origin of the other mode may be related to the space charge accumulated at the interface between liquid crystal and the polymer coating. In antiferroelectric liquid crystal (SmC_A^*) phase two switching current peaks were observed only in a $3\mu\text{m}$ thick cell by applying triangular wave of frequency around 30 Hz-40 Hz. Two antiferroelectric modes were obtained in the dielectric spectra of SmC_A^* phase in the low frequency region and the results have been discussed. Both the results of spontaneous polarization and dielectric studies reveal that the antiferroelectric behavior in the SmC_A^* phase is squeezed in each of the three cells.

Keywords: Ferro and anti-ferro electric liquid crystal; Electro-optic; Dielectric spectroscopy; Space charge mode

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INTRODUCTION:

Ferroelectric liquid crystals (SmC^* phase) exhibits two types of collective modes. The fluctuation of the tilt angle θ is known as soft mode and that of azimuthal angle ϕ is known as Goldstone mode ^[1-5]. In SmC^* phase soft mode can be detected only in the vicinity of $\text{SmC}^* \rightarrow \text{SmA}$ phase transition when the Goldstone mode is suppressed by DC bias electric field. In a finite thickness of the cell besides soft and Goldstone mode there are other low frequency modes such as domain modes ^[6,7] which have been attributed to the formation of the surface and bulk ferroelectric domain under the application of DC bias field. At frequencies less than 1kHz a very strong mode is observed and is attributed to the accumulation of space charge on the interfaces between the liquid crystal and the polyamide layer coated on the glass surface ^[8] and thickness mode ^[9].

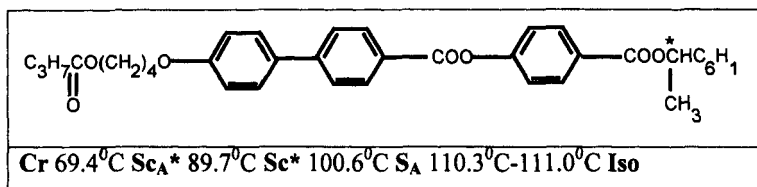
Since the discovery of the anti-ferroelectricity in chiral liquid crystal materials, many of its interesting properties have been studied by different groups ^[10-15]. Tilt of the molecules in the adjacent layers of anti-ferroelectric smectic C phase (SmC_A^*) are oppositely directed and there is no net polarization. In the anti-ferroelectric SmC_A^* phase two modes are usually observed in a planar oriented cell and are distinguished with respect to the respective critical relaxation frequency. High frequency mode around $10^5 \rightarrow 10^6$ Hz is usually regarded as being due to an antiphase motion of molecules in adjacent layers ^[16]. Another mode around 10^4 Hz -10^5 Hz corresponds to the rotation around the short axis ^[17-18]. Sometimes a mode was observed

around 1 kHz referred to as Goldstone like mode arises due to residual helical super-structure ^[19].

So far not too many works have been published on the thickness dependence of the various modes in the SmC_A* and SmC* phases. In this paper we have studied the electro-optic and dielectric properties of an anti-ferroelectric liquid crystal as a function of cell thickness and bias field.

EXPERIMENTAL

The material has been synthesized by Dabrowski. The structure and corresponding phase sequence of the material is shown below. It should



Scheme 1: Schematic diagram of the structure and corresponding phase sequence of the studied molecule.

be mentioned here that the phase sequence strongly depends on the purity of the sample and to some extents on the cell thickness. The phase transition temperatures were obtained by polarized light microscopy as well as by differential scanning calorimeter. The DSC trace of the compound is given in Fig.1. Measurements of the spontaneous polarization (P_s) and dielectric permittivities were made in 3 μ m, 6 μ m

and 10 μm thick (EHC) planar aligned cells. The dielectric measurements in the frequency range 10 Hz to 13 MHz were recorded using an

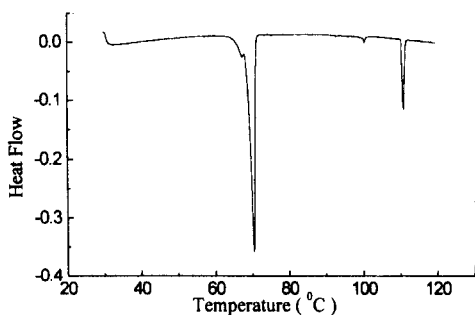


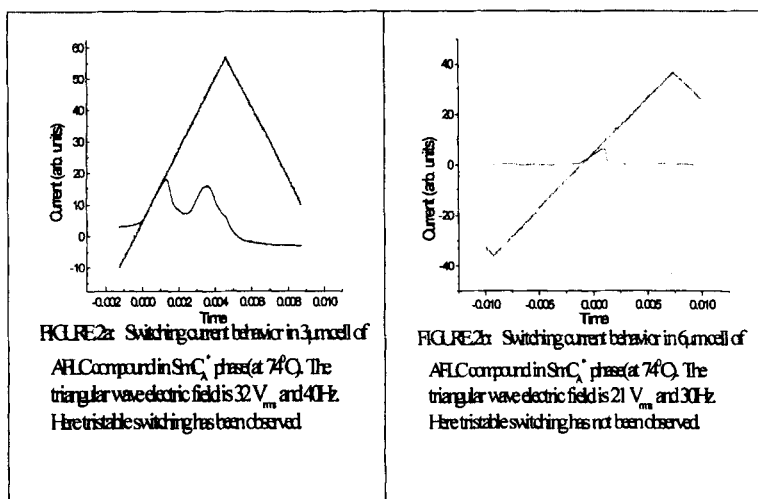
FIGURE.1: DSC curve taken with -5deg/min on cooling

Impedance Analyzer (HP 4192A) and which was controlled by a computer. The P_s measurements monitor the total induced polarization when the sample is switched to a saturated state. The measurements were carried using a planar aligned cell by applying low frequency triangular wave and spontaneous polarization has been determined by a straightforward current peak integration method. Characteristic dielectric parameters such as relaxation frequency and dielectric strength were obtained by fitting the data in cole-cole function for single and double relaxation processes.

RESULTS AND DISCUSSIONS:

Electro Optical properties

Switching current measurements were made in SmC_A^* and SmC^* phase to study the switching characteristics as well as to determine the spontaneous polarization. Two current peaks were observed in every half period of the applied voltage as shown in Fig. 2a in the range of temperature between $70^\circ\text{C} - 80^\circ\text{C}$ only in a $3\mu\text{m}$ thick cell, suggesting



antiferroelectric behavior in this region^[18], though DSC scan shows that the temperature of transition from $\text{SmC}^* \rightarrow \text{SmC}_A$ is around 90°C . The switching current in $6\mu\text{m}$ and $10\mu\text{m}$ thick cells exhibits single current peak (Fig. 2b) throughout SmC^* and SmC_A^* phases. The temperature dependence of spontaneous polarization at the cells of various thickness is shown in Fig. 3. The magnitude of P_s decreases with the decrease of

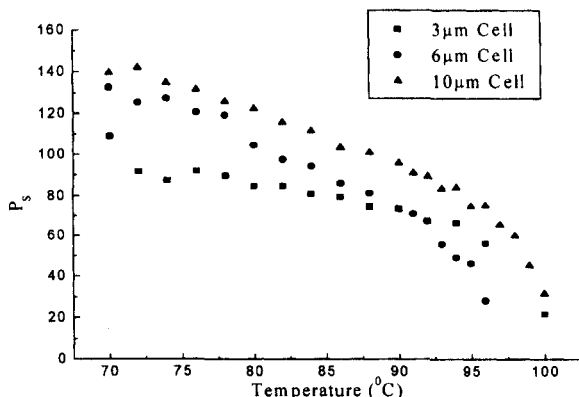


FIGURE.3: Spontaneous polarization changes with temperature in cells of different thickness. Here we can see the dependence on thickness

cell thickness provided the measuring electric field per unit thickness of the cell remains same. The results are in good agreement with a theoretical relation earlier developed ^[20,21] considering thickness, anchoring energy of the cell and elastic module. Tilt angle was measured using polarizing microscope in a 6 μm planar aligned cell. The saturated value of the cone angle at 70°C is 72° and that at the phase transition is 12°.

Dielectric Measurements:

Frequency dependence of the dielectric loss curve in a 10 μm thick sample in the SmC* phase exhibits two relaxation processes, referred to as mode1 and mode2, in this paper and are shown in fig. (4). The relaxation frequency of mode1 is around 70Hz and that of mode2 is around 900Hz and their relaxation strengths are of the same order. The

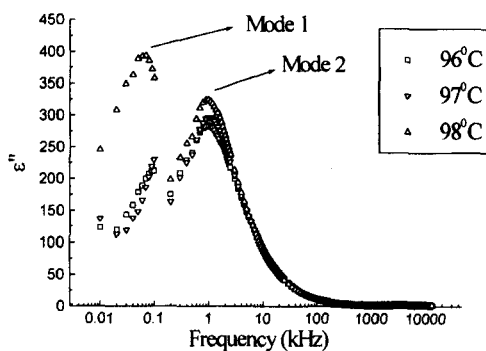


FIGURE.4: Dielectric loss as a function of temperature. Measurements were made in a $10\mu\text{m}$ thick cell at three different temperatures in SmC^* phase. Here two modes were detected.

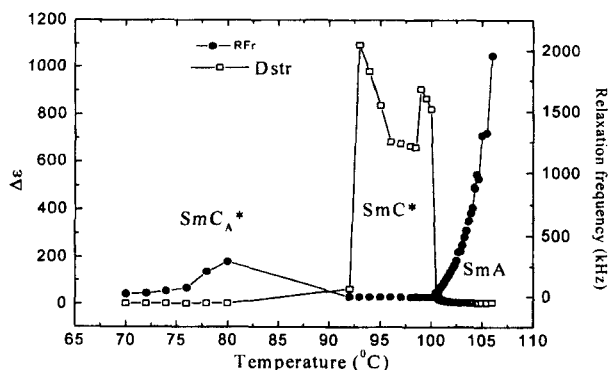


FIGURE.5: Temperature versus Strengths and Relaxation freq. in various phases in a $10\mu\text{m}$ thick cell.

dielectric strength of mode2 slowly decrease with increase of temperature and finally in the vicinity of SmC^* - SmA transition temperature, the strength increases to a high value and then sharply drops at T_C . Thus mode2 behaves like Goldstone mode. Model1 exists

throughout SmC* phase and its origin is still not very clear, may be due to space charge accumulation on the interfaces between liquid crystal and polyamide coating and there is no relation to any structural motion. Relaxation strength of both mode1 and mode2 rapidly decrease with the application of D.C. bias field. In case of mode2, it is clearly due to unwinding of helix, but in case of mode1, when a dc bias field is applied the accumulated space charge remained bound at the interface and as a result the dielectric strength rapidly drops to a minimum value with the increase of bias field. Temperature dependence of Soft mode dielectric strength $\Delta\epsilon_s$ in a 10 μm , 6 μm and 3 μm thick sample has been determined in SmA phase. The soft mode strength as usually decreases with the increase of temperature as shown in Fig. (6). The temperature dependence of the inverse of $\Delta\epsilon_s$ follows the Curie Weiss law. The temperature of transition (T_C) from SmA phase to any higher ordered phase has been determined from the intersection of inverse of the soft mode dielectric strength with temperature axis. Temperature of transition from SmA to SmC* phase (T_C) in 10 μm and 3 μm thick cells have been determined from dielectric method and is almost the same as that obtained from DSC curve. The dielectric strength of Goldstone mode in a SmC* phase is remarkably high and relaxation frequency is relatively low compared to structurally similar compound^[22] having almost same spontaneous polarization. The high strength of Goldstone mode of this compound means less restoring power of the helicoid, a less restoring power and low relaxation frequency indicate a long helical pitch in SmC* phase of this compound.

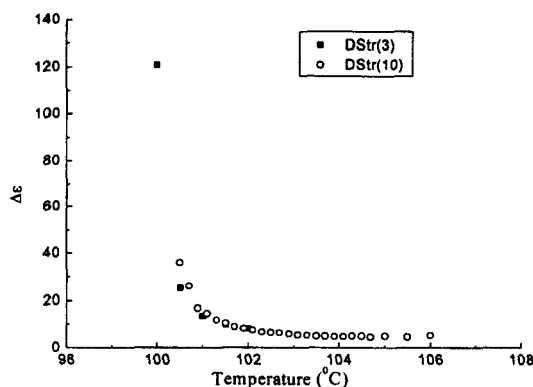


FIGURE.6: Dielectric strength varies with temperature in $3\mu\text{m}$ & $10\mu\text{m}$ thick cells. In $3\mu\text{m}$ thick cell the soft mode disappears much quickly than in $10\mu\text{m}$ thick cell.

Dielectric properties in SmC_A^* phase in a planar aligned cell is shown in Fig. (7). Two distinct absorption region specifying two relaxation processes were observed in SmC_A^* phase. At low frequency one process was observed around 30-40kHz in each of the 3 cells and another process was observed at still lower frequency around 1kHz (Fig.7) in a $3\mu\text{m}$ thick cell. Temperature dependence of relaxation frequency and relaxation strength is shown in Fig (8&9). These parameters weakly depend on temperature. Considering the weak temperature dependence of relaxation frequency and strength, the low frequency anti-ferroelectric mode that obtained around 30-40kHz may be attributed either due to reorientation around short axis of the molecule as proposed by Uehara et al. or it may be due to collective

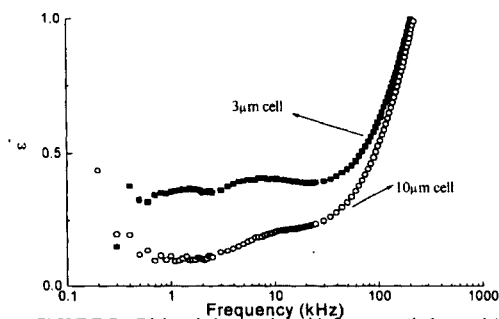


FIGURE.7: Dielectric loss varies with frequency(in log scale) for $3\mu\text{m}$ and $10\mu\text{m}$ thick cells. A common mode have been observed, nearly at 10kHz , in both the cells. But another mode has been observed in $3\mu\text{m}$ cell nearly at 1kHz .

reorientation of the molecules in the same phase (in phase motion) around the cone as proposed by Buivydas *et al.* and lower frequency mode that obtained at 1kHz may be assigned as Goldstone like mode arises due to a residual helicoidal super structure on cooling from the SmC^* phase as earlier mentioned by different workers^[17,18]. It should be noted here that Fofara *et al* observed the above mentioned anti-ferroelectric modes of this compound in comparatively lower frequencies. They have used gold plated cells and no aligning agent has been used for the measurement. On the other hand we have used polyamide rubbed ITO coated plate for the measurement and due to surface anchoring the relaxation frequency may have been shifted towards higher frequency. It has been discussed in an earlier section that the polarization current shows two current peaks in every half period of the applied triangular wave in the range of temperature between 70°C to 80°C only in a $3\mu\text{m}$ thick cell and with further increase of temperature from 80°C up to para-electric phase switching current

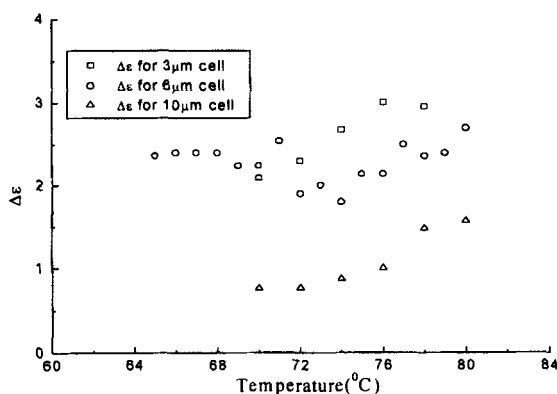


FIGURE.8: Dielectric Strength($\Delta\epsilon$), in SmC_A^* phase, varies with temperature. The graph shows the variation of $\Delta\epsilon$ for the three cells.

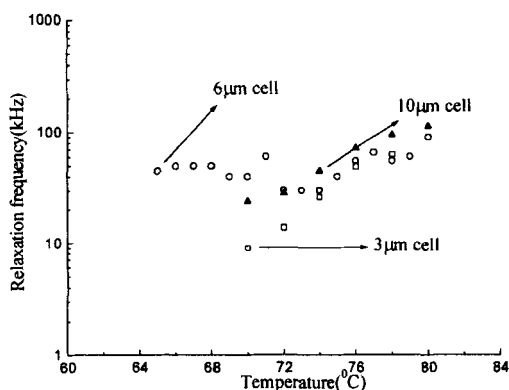


FIGURE.9: Relaxation frequency varies with temperature in SmC_A^* phase. The plot shows the variation of Relaxation frequency for above mentioned cells of three different thickness.

exhibits single current peak. Moreover no anti-ferro nor ferro electric modes were observed in the range of temperature between 80°C to 90°C , although polarizing microscopy and DSC studies show a SmC_A^* phase in the above range of temperature. So the above result suggests

that the SmC_A^* phase is either squeezed in thin cells as reported earlier by Lagerwall *et al.* or the temperature in SmC_A^* phase, while approaching towards SmC^* phase the SmC_A^* pitch becomes longer, the molecules in adjacent layers are exactly 180° angle to each other. Therefore the polarization in adjacent layers cancel and no net polarization appears. The anti-ferroelectric mode thus becomes inactive in range of temperature between 80° to 90°C .

CONCLUSIONS:

Two relaxation processes have been detected in SmC^* phase, one is Goldstone mode process and other is related to space charge accumulation at the interface between polymer substrate and liquid crystal molecules. Two anti-ferroelectric modes were observed in the low frequency region of SmC_A^* phase. The results of spontaneous polarization and dielectric studies reveal that the antiferroelectric behavior in SmC_A^* phase is squeezed in $3\mu\text{m}$, $6\mu\text{m}$ and $10\mu\text{m}$ thick cells.

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