SUMMARY OF THE THESIS ON

CHARACTERIZATION OF FERRO- AND ANTIFERRO-ELECTRIC LIQUID CRYSTALS

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Liquid crystal (LC) is a fascinating state of matter which possesses mechanical properties and molecular packing arrangements in between those of a liquid and a crystal. The liquid crystal materials are mainly classified as thermotropic and lyotropic. Lyotropic liquid crystals show the transitions as an effect of the solvents and these LCs are of great interest biologically and appear to play an important role in living systems. However, thermotropic liquid crystals are the focus of this research work and exhibit phase transitions affected by the change in temperature. Thermotropic LCs are mostly made of the rod shaped molecules. Generally LC phases are classified into two categories viz. nematics and smectics. In the nematics, the molecules put together into layers maintaining themselves parallel to each other in a particular direction represented by a unit vector \( \hat{n} \) called director such that they possess long range orientational order around \( \hat{n} \) and some sort of short range positional order as well. The smectics phases are divided in several subphases viz. SmA\(^*\), SmC\(^*\)\(_{\alpha}\), SmC\(^*\)\(_{\beta}\), SmC\(^*\)\(_{\gamma}\), SmC\(^*\)\(_{\Lambda}\) and SmI\(^*\)\(_{A}\) etc. The symbol * as a superscript with each subphases refers to the chirality of molecules. In the SmA\(^*\) phase the average direction of the molecules, i.e., \( \hat{n} \) is parallel to the layer normal whereas in the SmC\(^*\) phase the molecules are tilted with respect to \( \hat{n} \) and smectics layer normal \( \hat{k} \). The tilt is defined as the tilt angle \( \theta \). The subphases SmC\(^*\)\(_{\alpha}\), SmC\(^*\)\(_{\beta}\), SmC\(^*\)\(_{\gamma}\) and SmC\(^*\)\(_{\Lambda}\) are particular cases of the SmC\(^*\) phase. The chirality of the molecules induces slight rotation from layer to layer in the tilting of molecules resulting in a helical structure in the SmC\(^*\) phase. As a consequence the spontaneous polarization \( \vec{P}_S \) is associated with each smectic layer perpendicular to the \( \hat{c} \) director and layer normal \( \hat{k} \) which makes the phase ferroelectric in nature. The helical structure is characterized by a pitch where the molecule after rotation in each smectic layer along \( \hat{k} \) attains its original position. On average in the SmC\(^*\) phase there occurs a macroscopic spontaneous polarization within a pitch. On the other hand if the molecules forming SmC\(^*\) phase possess significantly large transverse permanent electric dipole moment on the end chains thereby a relatively large spontaneous polarization, then antiferroelectric chiral smectic C (SmC\(^*\)\(_{\Lambda}\)) phase may result at
lower temperature side. Unlike the SmC\(^*\) phase, in the SmC\(^*\)_A phase the molecules in the consecutive layers are tilted in the opposite direction with respect to the layer normal. Therefore, the polarization vectors in the adjacent layers, being in opposite direction, are cancelled out which implies lack of macroscopic spontaneous polarization. The phase possesses antiferroelectricity.

These various liquid crystals phases are advantageous for displays. Ferroelectric liquid crystals (FLCs) have features like fast response time, and wide viewing angles, which makes it attractive for their use in the flat panel displays. However, FLCs suffer some drawbacks. Some main problems for the practical application of FLC displays are the insufficient threshold, insufficient contrast (due to chevron defects), and insufficient bistability due to difficulty in controlling alignment, the low mechanical stability of the molecular orientations and the achievement of desired gray scale.

For the first time in 1989, antiferroelectric liquid crystals (AFLCs) with good electro-optical properties are considered as a promising material for display devices by Chandani. AFLCs are now regarded as an attractive alternative to FLCs for quality multimedia displays with high resolution due to their tristate switching behavior (double hysteresis), easy dc compensation, microsecond response, hemispherical viewing angle, no ghost effect, grey scale capability and ability of multiplexing in passively addressed matrices. They also exhibit thresholdless, hysteresis free and V-shaped switching. Despite all these attractive electro-optic features, their commercial production is hindered due to pretransitional effects and the perfect dark state problem. This problem can be overcome by using AFLCs having high tilt angle of approximately 45° commonly known as orthoconic antiferroelectric liquid crystals (OAFLCs).

Along with their technological importance, discovery of AFLCs has also attracted much attention of researchers from the point of view to understand their fundamental structure and properties due to their richness of phases such as SmA\(^*\), SmC\(^*\) and SmC\(^*\)_A etc in between isotropic and crystal phases. Several studies such as thermodynamic, electro-optical, optical, dielectric, switching and conoscopic etc have been done till date for AFLCs. With dielectric study many relaxation modes have been reported in various phases of the AFLC materials. Soft mode (SM) associated
with the tilt fluctuations of the directors have been found to exist mostly in the SmA* phase and near the transition region of the SmA*—SmC* phase. The SmC* phase is commonly known to show the Goldstone mode (GM) with dielectric study. On the other hand the SmC* A phase is characterized by two well known high kHz and low kHz antiferroelectric modes, the origins of which is still an issue of thought. The various new relaxation modes are also found in the SmC* and SmC* A phases on the application of DC bias. However, the cause of these relaxation modes is not suggested yet and the variation of their characteristic dielectric parameters such as dielectric strengths ($\Delta \varepsilon$) and relaxation frequencies ($f_R$) with the bias electric field and temperature have been found rarely. Also the thickness effect on these relaxation modes has also not been much studied earlier. Hence, in the light of above discussion a highly tilted (~45°) chiral AFLC material \((S)-4-(1\text{-methylheptyloxycarbonyl)}\) phenyl-4’-(6-pentanoyloxyhex-1-oxy) biphenyl-4-carboxylate [4H6Bi(S)] synthesized by Dabrowski’s group of Institute of Chemistry, Military University of Technology, Warsaw 00-908, (Poland), has been chosen. The molecular structure of the material is as follows:

\[
\text{C}_4\text{H}_9\text{COO(CH}_2\text{)}_6\text{O} \quad \text{COO} \quad \text{COO} \quad \text{HC}_6\text{H}_{13} \quad (S) \\
\text{CH}_3
\]

The thermodynamic, optical, dielectric and switching studies for this material have been performed and the characteristic parameters regarding these studies have been estimated and presented here. The dielectric study has been performed by varying temperature, bias for two cell thickness (10 $\mu$m and 4 $\mu$m). Switching study has been done by the polarization reversal current technique. From the thermodynamic and optical polarizing microscopic studies the molecule is found to possess the following phases with corresponding transition temperatures at 10 °C/min:

\[
\text{Cr} \rightarrow (64.8 \, ^\circ\text{C}) \rightarrow \text{SmC}^* \rightarrow (93.5 \, ^\circ\text{C}) \rightarrow \text{SmC}^* \rightarrow (96.2 \, ^\circ\text{C}) \rightarrow \text{SmA}^* \rightarrow (101.8 \, ^\circ\text{C}) \rightarrow \text{Iso}
\]

In spite of the chiral molecules it was also intended to carry out these studies for the racemic AFLC materials also. Since for the application of AFLCs the helix
should not be present there in the material. The racemic materials are expected to be free from helix because of mixing of its two enantiomers (which are oppositely optical handed) in the equal ratio. Thus a racemic material (R,S)-4’-(1-methylheptyloxyxycarbonyl)biphenyl-4-yl 4-[3-(2,2,3,3,4,4,4-heptafluorobutoxy)prop-1-oxyl]-2,3-difluorobenzoate has been chosen which is also synthesized by the same Dabrowski’s group. The molecular structure of this material with the phase transition temperatures 10 K/min and phase sequence is given below:

\[
\begin{align*}
\text{Cr}_2 & \leftarrow (36.4) \rightarrow \text{Cr}_1 \leftarrow (49.8) \rightarrow \text{SmC}_A \leftarrow (96.5) \rightarrow \text{SmC} \leftarrow (99.4) \rightarrow \text{Iso}
\end{align*}
\]

For this material the thermodynamic, optical and the temperature dependent dielectric spectroscopy has been carried out.

Thermodynamical study of liquid crystal materials/mixtures of different concentrations is made using two Differential Scanning Calorimeters (DSC): (i) DSC of NETZSCH (model DSC 200 F3 Maia) and (ii) Perkin Elmer DSC (model DSC-7), which has a built-in-software (Pyris) to determine the peak transition temperatures, the onset temperatures and the transition enthalpies. For the optical and dielectric studies of LCs, the measuring cell is taken in the form of parallel plate capacitor made from ITO coated conducting glass plates of sheet resistance 25 Ω/ separated by mylar spacers of different thicknesses under planar and homeotropic geometry. The same cell for the planar alignment is used for the study of switching properties. The temperature of the sample is controlled with the help of a hot stage of Instec (model HS1). Textures of different phases of the materials are identified by using the polarizing microscope of CENSICO (model IZUMI 7626) equipped with a built-in-white-light source at the base. Dielectric studies have been carried out with the help of two impedance/gain-phase analyzers: (i) Hewlett-Packard (model 4194A) and (ii) Solartron Bridge (model SI1260) coupled with Solartron dielectric interface (model-
Solartron has been used for low frequency measurement especially below 100 Hz.

The measured data was analyzed using generalized Cole-Cole equation, which is written as

\[ \varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon'(\infty) + \sum_i \left( \frac{(\Delta\varepsilon_i)}{1 + \left(j\frac{f}{f_R^i}\right)^{h_i}} \right) + \frac{A}{f_n^m} - j\frac{\sigma_{\text{ion}}}{2\pi\varepsilon\varepsilon_0^k} - jBf^m \]  

where, \( \Delta\varepsilon = \varepsilon'(0) - \varepsilon'(\infty) \) is the dielectric strength; \( \varepsilon'(0) \) and \( \varepsilon'(\infty) \) are the low and high frequency limiting values of the relative permittivity respectively. \( \varepsilon_0 \) (= 8.85 pF/m) is the free space permittivity. \( f_R \) and \( h \) are relaxation time (inverse of the angular relaxation time \( \tau \)) and distribution parameter (0\( \leq h \leq 1 \)). The suffix \( i, \) used for various parameters, corresponds to the \( i^{th} \) mode respectively. The 3\( \text{rd} \) and 4\( \text{th} \) terms of the above equation represent the contribution of electrode polarization capacitance and ionic conductance (\( \sigma_{\text{ion}} \)) at low frequencies respectively where, \( A, n \) and \( k \) are fitting parameters. In case of pure ohmic conductivity, \( k=1 \). An additional imaginary term \( Bf^m \) is empirically added in Eq. (1) to partially account for these contributions where, \( B \) and \( m \) are fitting constants. The measured dielectric loss (\( \varepsilon'' \)) contains contributions due to finite resistance of ITO coated electrodes, inductance of leads and capacitance above 100 kHz.

The thermodynamic and optical polarizing microscopy studies of the material 4H6Bi(S) confirms the existence of SmA\( ^* \), SmC\( ^* \) and wide temperature ranged SmC\( ^* \_A \) phases in the order of their appearance respectively between the isotropic and crystal phases. From the dielectric spectroscopy it has been investigated that SmA\( ^* \) phase of the material exhibits SM with temperature dependent relaxation frequency varying from 530 to 60 kHz and dielectric strength from 0.06 to 7.0. SM mode is also observed in the SmC\( ^* \) phase upto 1 °C below SmA\( ^* \)–SmC\( ^* \) transition temperature with dielectric strength decreasing from 7 to 4. \( \Delta\varepsilon_\perp \) and \( f_R \) of the SM are found to be almost independent of cell thickness. To ensure planar alignment of the material the subscript \( \perp \) is used with \( \Delta\varepsilon \). The SmC\( ^* \) phase shows GM which is related to fluctuations in the phase angle having temperature independent relaxation frequency and very high dielectric strength which is highly temperature dependent. The \( \Delta\varepsilon_\perp \) of
GM is found to decrease significantly from 195 to 69 whereas, its $f_R$ is found to increase from 2 kHz to 4 kHz with the decreasing cell thickness. The decrement in the $\Delta \varepsilon_{\perp}$ of the GM for the lower cell thickness is because of the partial helix suppression in the SmC$^*$ phase due to increased surface interaction on the molecular arrangement near the electrode plates. The increase in the $f_R$ with decreasing cell thickness is due to the need of more energy to overcome the restriction imposed by the surface interaction on the winding and unwinding motion of the helical structure arising because of the electric field. The GM is suppressed with DC bias at a critical bias voltage of 6.0 V. This critical bias voltage of the SmC$^*$ phase for the helix unwinding is independent of cell thickness. Dielectric spectroscopy suggests that by the application of DC bias, SM can be made to appear in that temperature region of the ferroelectric phase (SmC$^*$) where it is not observed in the absence of DC bias. The $\Delta \varepsilon_{\perp}$ of SM first increases till complete suppression of the GM and then decreases with the increasing DC bias whereas its $f_R$ does not depend on the DC bias. In the SmC$^*$ phase besides the GM and SM, one more low frequency mode (LFM), having its $\Delta \varepsilon_{\perp}$ comparable to that of the GM ($\sim$195), is investigated in the frequency range 35-45 Hz for the 10 $\mu$m thick cell. However, the $\Delta \varepsilon_{\perp}$ and $f_R$ of LFM shows their dependence on the thickness in a manner opposite to that of the GM, i.e., $\Delta \varepsilon_{\perp}$ increases upto $\sim$334 but $f_R$ decreases and lies in the frequency range 1-10 Hz for the 4 $\mu$m thick cell. This LFM is correlated to the azimuthal pretilt angle distortion. Domain mode (DM) arises in the absence of helix in the SmC$^*$ phase due to formation of periodic modulated structures which are formed by the modulation of in-layer plane polarization vectors along the electric field direction. The $\Delta \varepsilon_{\perp}$ of DM decreases whereas relaxation frequency increases with decreasing cell thickness (from 100 Hz for the 10 $\mu$m and 3 kHz for the 4 $\mu$m thickness) but both are almost invariant with the DC bias. Two antiferroelectric modes of dielectric relaxation AFM1 and AFM2 have been observed in the SmC$^*$ phase whose $f_R$ varies from 600–190 kHz and from 100 –1.5 kHz respectively. The $\Delta \varepsilon_{\perp}$ of AFM1 is temperature independent whereas that of AFM2 is temperature dependent. Thus, relaxation frequencies of both the relaxation modes show the temperature dependence and follow the Arrhenius behaviour and can be fitted to the Arrhenius equation.
\[ f_R = f_0 \exp(-E_a/kT) \]  

where, \( f_0 \) is a constant, \( E_a \) is the activation energy, \( k = 1.38 \times 10^{-23} \text{ J-K}^{-1} \) is the Boltzmann constant and \( T \) is the absolute temperature. From the Arrhenius plot the activation energies of modes AFM1 and AFM2 are obtained as 42 kJ/mol and 107 kJ/mol respectively. On the application of DC bias it has been found that the \( \Delta \varepsilon \) of mode AFM1 is invariant up to 6.0 V and then increases onwards and found to be slightly varying with the cell thickness whereas, \( \Delta \varepsilon \) of mode AFM2 slightly increases with increasing bias voltage and is approximately same for both the thicknesses. However, an interesting feature is observed for the 4 \( \mu \)m thick cell that the \( \Delta \varepsilon \) of mode AFM1 decreases for the bias voltages greater than 24.0 V which was not observed for the 10 \( \mu \)m thick cell. This behaviour of mode AFM1 is similar to the suppression of GM with the bias voltage. On the other hand, it has also been observed that relaxation frequencies of the antiferroelectric modes AFM1 and AFM2 are found to be independent of DC bias and cell thickness. Therefore, from the thickness and bias field dependent dielectric studies the high frequency antiferroelectric mode (AFM1) is assigned to antiphase antiferroelectric Goldstone mode and the low frequency mode (AFM2) to the anti tilt azimuthal angle fluctuation mode. A field induced mode (AFM3) is found to exist in the SmC*_A phase on the application of DC bias which arises at 11.0 V for 10 \( \mu \)m and at 8.0 V for 4 \( \mu \)m cell thicknesses. The \( \Delta \varepsilon \) of mode AFM3 shows increasing behaviour up to 29.0 V for 10 \( \mu \)m thick sample and up to 17.0 V for 4 \( \mu \)m thick sample but beyond these DC voltages, \( \Delta \varepsilon \) decreases. However, the \( f_R \) of mode AFM3 increases constantly from 100 Hz to 600 Hz for 10 \( \mu \)m thick cell and from 175 Hz to 1 kHz for 4 \( \mu \)m thick cell with increasing bias voltage, i.e., its magnitude as well as rate of increase are greater for the 4 \( \mu \)m thick cell. It can be noted that the mode AFM3 is induced by the field in the pretransitional regime of the AFLC material and also AFM3 seems to be suppressed with increasing DC voltage as well as its \( f_R \) is found to increase for the lower thickness. This behaviour of \( \Delta \varepsilon \) and \( f_R \) of AFM3 is like the variation of characteristic dielectric parameters of GM with bias and cell thickness. Therefore, mode AFM3 is assigned to the field induced antiferroelectric Goldstone mode. In the very low frequency region between 2-5 Hz, one relaxation mode of very weak
dielectric strength is observed above 20.0 V for the 10 µm thickness and is not observed for the 4 µm thickness. This mode belongs to the switch mode.

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>FLC phase</th>
<th>AFLEC phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_S$ (nC cm$^{-2}$)</td>
<td>$t_S$ (ms)</td>
</tr>
<tr>
<td>FLC#252</td>
<td>8–104</td>
<td>2–36</td>
</tr>
<tr>
<td>MHPB(H)PBC</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>W-132A</td>
<td>1–20</td>
<td>–</td>
</tr>
<tr>
<td>W-193B-I</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>W-201</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MOPB(H)PBC</td>
<td>58–120</td>
<td>–</td>
</tr>
<tr>
<td>AFLC mixture</td>
<td>50–71</td>
<td>–</td>
</tr>
<tr>
<td>C$_2$F$_2$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4H6Bi(S) [present work]</td>
<td>70–105</td>
<td>2–4</td>
</tr>
</tbody>
</table>

Table 1: Switching parameters for FLC and AFLC phases of some FLC and AFLC materials.

The switching study of the material 4H6Bi(S) material gives the increase in critical electric field $E_C$ (needed for the complete unwinding of the helix) from 2.0 to 6.0 in the SmC$^*$ phase and from 15.0 to 92.0 in the SmC$^{*A}$ phase with the decreasing temperature. This increase may be so, because the anti-tilt pairing of the dipoles in the helical structure is stronger in the SmC$^{*A}$ phase than the SmC$^*$ phase. That’s why more energy is needed for the unwinding process in the SmC$^{*A}$ phase and hence, more the critical electric field. The torsional viscosity ($\gamma_t$) increases with the decreasing temperature and the maximum value of $\gamma_t$ is 16.4 Pa·s at 58.2 °C in the SmC$^{*A}$ phase. The value of spontaneous polarization ($P_S$) increases from SmC$^*$ to SmC$^{*A}$ phase according to the power law $P_S = P_0(1-(T/T_C))^\beta$ with $\beta = 0.37$ indicating the first order paraelectric to ferroelectric phase transition. $P_S$ is found to be high (maximum value ~235.0 nC/cm$^2$) in the SmC$^{*A}$ phase at lowest temperature which is higher than the other protonated AFLC materials such as MHPB(H)PBC, MOPB(H)PBC and some mixtures also. Switching time ($t_S$) of this material is found
to be very small and varying from 2 ms to 4 ms in the SmC* phase but falls from 4 ms to 0.4 ms at the SmC*–SmC_A phase transition and again shows variation from ~0.4–0.7 ms in SmC_A phase. This increase in t_S in each helical phase with the decrease of temperature is the consequence of increase in viscosity with the decreasing temperature. The value of t_S is small as compared to other FLC and AFLC materials listed in the Table-1. From the comparison of the various switching parameters listed in Table-1, the material 4H6Bi(S) appears to be better material suited for applications in display devices due to higher value of \( P_s \), low switching time (microsecond response) and having two tilted switchable smectic phases.

With the thermodynamic, texture and dielectric studies of the racemic AFLC material (R,S)-4′-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-[3-(2,2,3,3,4,4,4-heptafluorobutoxy)prop-1-oxyl]-2,3-difluorobenzoate is found to exhibit a non chiral SmC phase and a large temperature ranged non chiral SmC_A phase. The chirality destroys because of the mixing of the R and S enantiomers in 1:1 ratio. From the dielectric spectroscopy it has been investigated that the relaxation mode M1 observed in the SmC phase possesses very small but slightly increasing \( \Delta \varepsilon_\perp \) from ~0.2–0.54 and decreasing \( f_R \) varying from 45.5–16.3 kHz in the temperature interval 97.8–89.6°C. This mode is assigned to the domain mode. In the SmC_A phase two relaxation modes M2 and M3 are detected. M2 is the same as M1 which continues from the SmC phase but due to showing different behaviour as compared to M1 and also distinguishing it from M1 in the SmC_A phase it is abbreviated as M2. With the decreasing temperature, it shows small \( \Delta \varepsilon_\perp \) varying from ~0.6-1.0 and linearly decreasing \( f_R \) from 16.2 kHz to 6.0 Hz throughout the SmC_A phase. This relaxation mode is believed to be associated with the tilt fluctuation of the directors in their anti-tilt pairs. The other mode M3 in the SmC_A phase appears in the MHz region at 48.0°C. Its \( \Delta \varepsilon_\perp \) increases more rapidly from 0.2–3.5 as compared to the other modes. However, its \( f_R \) shifts towards lower frequency side continuously from 1.2 MHz to 522 kHz. Due to the appearance of this mode at the MHz region, this is supposed to arise due to molecular rotation along their long axis. For this material also the relaxation frequencies of all the relaxation modes follow the Arrhenius equation (1)
as described above. The activation energies of all the three modes M1, M2 and M3 calculated from the Arrhenius equation of the relaxation frequencies are 148.0 kJ/mol, 115.5kJ/mol and 62.5kJ/mol respectively.