CHAPTER 6

INDUCTION AND ENHANCEMENT OF FERROELECTRIC SMECTIC C* PHASE IN MULTI - COMPONENT ROOM TEMPERATURE MIXTURES

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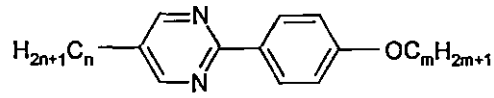
*Part of the work was presented in the International Conference on Liquid Crystals in the Department of Physics, University of Mumbai, December 2012 and was published in Japanese Journal of Applied Physics 48 (2009) 011501 and Molecular Crystals and Liquid Crystals, Vol. **547**, P. 25-32, 2011.*

6.1. INTRODUCTION

Since the discovery of the ferroelectric liquid crystal (FLC) compound 4-decyl-oxybenzylidene-4′-amino-2-methylbutyl-cinnamate (DOBAMBC) and antiferro-electricity in 4-(1-methylheptyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC) [59,348], FLCs have been the subject of intense investigation not only for their intriguing properties for fundamental condensed matter research, but also for their application in fast switching flat panel displays, optical light modulators, optical signal processing and computing [316]. This family of materials combines the ferroelectric, electrooptic, piezoelectric and pyroelectric properties of solid polar dielectric materials with the physical flow characteristics of liquids. However FLC materials for optoelectronic applications must have the following spectrum of physical properties tailored to the specific application: broad temperature range from or below ambient temperature, rise time, birefringence, clarity, polarization, tilt angle, length of pitch, and thermal and UV stability [349,350]. In general, no single FLC compound can satisfy all the above requirements. For example, FLC compound DOBAMBC melts at 76^0C [351] and the melting point for AFLC compound MHPOBC is 84^0C [352] and as such not useful for any consumer devices. Multicomponent mixtures are, therefore, formulated to optimize all the required properties for practical applications. For this one has to select proper host materials, which controls the temperature range and tilt angle; chiral dopants to control the switching speed and helical pitch and birefringence dopants to adjust the birefringence to the desired level [349]. While mixing materials one also has to keep in mind that physical properties of an individual material is often different in mixtures compared to its pure state because the intermolecular interactions are also different. Keeping these in view, several multicomponent FLC mixtures have been formulated which exhibit ferroelectric SmC* phase over a wide temperature range around room temperature.

6.2. EXPERIMENTAL PROCEDURE

For preparation of the mixtures two multi-component achiral base matrixes are used as hosts and three chiral compounds as dopants. For creating base matrixes non-chiral phenyl pyrimidine and biphenyl pyrimidine compounds were used to have tilted SmC phase at room temperature. Molecular structures of the mixing components are presented in **Figures 6.2.1.** Their phase behaviour and transition temperatures are given in **Table 6.2.1.**

(a) 

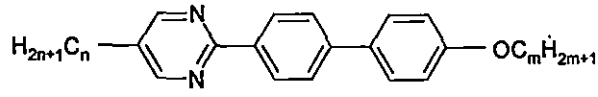
(b) 

Figure 6.2.1. Molecular structures of the components of hosts.

Host 1: Three non-chiral phenyl pyrimidine compounds **[Figure 6.2.1(a)]** and one non-chiral biphenyl pyrimidine compound **[Figure 6.2.1(b)]** with composition as noted below were mixed to formulate host mixture 1:

(a) i) n=8, m=6, 30% ii) n=8, m=8, 27% iii) n=8, m=9, 10%

(b) n=8, m=8, 33%

Host 2: Only three non-chiral phenyl pyrimidine compounds of **Figure 6.2.1(a)** with following members and compositions were mixed to formulate host mixture 2:

(a) i) n=8, m=6, 35% ii) n=8, m=8, 30% iii) n =10, m=8, 35%

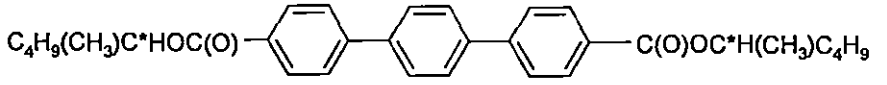
It is evident from **Table 6.2.1** that the overall mesophase stability and stability of individual phases are much larger in Host 1 compared to host 2.

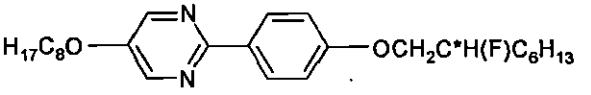
Following three different types of chiral compounds were used as dopants:

Dopant 1 (DOP1): Non-mesogenic chiral terphenyl compound with chiral centers at opposite ends **(Figure 6.2.2a)**.

Dopant 2 (DOP2): Singly fluorinated chiral phenyl pyrimidine compound exhibiting very small range monotropic **SmC*** phase with chiral center at one end **(Figure 6.2.2b)**.

Dopant 3 (DOP3): Singly fluorinated chiral phenyl pyrimidine compound exhibiting moderate range enantiotropic **SmC*** phase with chiral centers at opposite ends **(Figure 6.2.2c)**.

(a) 

(b) 

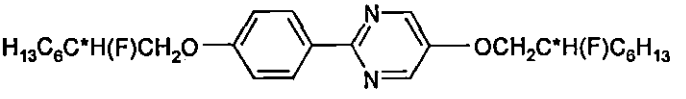
(c) 

Figure 6.2.2. Molecular structures of the dopants – DOP1 (a), DOP2 (b), and DOP3(c).

Six mixtures were formulated using the above two host mixtures and three dopants, compositions of the formulated mixtures were as follows:

LAHS1: Host1 + DOP1: 80% + 20%
LAHS2: Host2 + DOP1: 80% + 20%
LAHS3: Host2 + DOP2: 80% + 20%
LAHS4: Host1 + DOP3: 80% + 20%
LAHS5: Host2 + DOP3: 80% + 20%
LAHS6: Host2 + DOP1 + DOP3: 80% + 10% + 10%

Experimental procedure for measuring phase transition temperatures, X-ray photograph, dielectric and electro-optical study have already been discussed in chapter 5 in details.

Optical tilt of molecules in smectic layers was determined by measuring the angle of rotation of the analyzer between two extinction conditions while the sample was observed under a polarizing microscope in switching condition under a square wave of very low frequency (about 10 mHz). Response time of the sample was determined by measuring the time delay of occurrence of polarization bump from the applied square pulse edge (20Vpp, 10 Hz) while monitoring, in storage oscilloscope, the voltage across a resistor in series with the cell. Sample temperature was regulated by a Eurotherm controller 2216e within ± 0.1^0C in all measurements.

6.3. RESULTS AND DISCUSSION

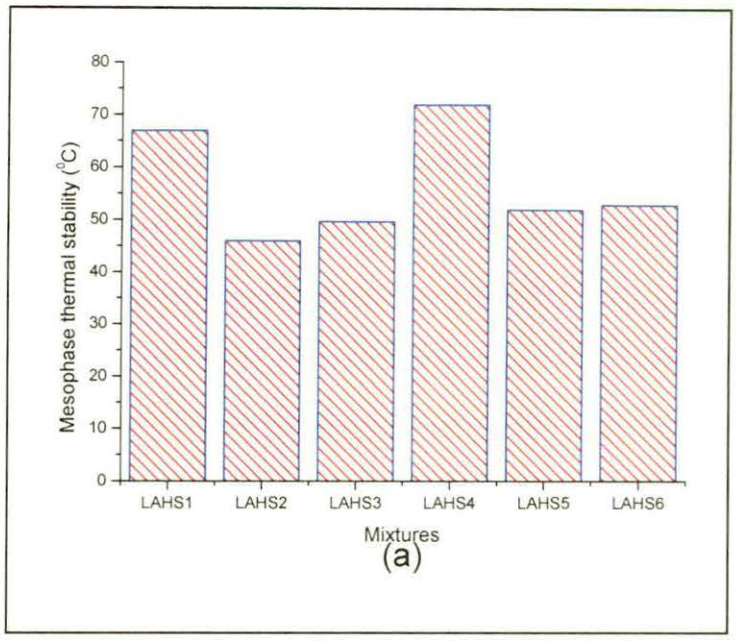
Six room-temperature FLC mixtures have been formulated. Thermal and phase behavior of the hosts, dopants and the mixtures as obtained by optical polarizing microscopy and dielectric experiments are given in **Table 6.2.1**. Characteristics of the observed phases are discussed below:

Table 6.2.1
Transition temperatures and thermal stabilities of different phases of the hosts, dopants and mixtures.

Sample	Transition temperature	Thermal stability(ΔT)
Host 1	Cr <20 SmC 70 SmA 79.2 N 100.2 I	>80(Meso) >50 (SmC) 9.2 (SmA) 21 (N)
Host 2	Cr <20 SmC 54.2 SmA 67.5 N 69.3 I	>49(Meso) >34.2(SmC) 13.3(SmA) 1.8(N)
DOP1	Cr 75 I	
DOP2	Cr 63.4 N 70.8 I I 70.6 N 62.4 SmC* 59.6 Cr	11 (Meso) 2.8(SmC*) 8.2 (N)§
DOP3	Cr 78 SmC* 89 SmA* 93.8 I I 93.5 SmA* 86 SmC* 66 Cr	27.5(Meso) 7.5(SmA*) 20(SmC*)§
LAHS1 (Host1+Dop1)	Cr <20 SmC* 80.6 SmA* 81.1 N* 87.0 I	>67(Meso) >60.6 (SmC*) 0.5 (SmA*) 5.9 (N)
LAHS2 (Host2+Dop1)	Cr <20 SmC* 58 SmA* 66 I	>46(Meso) >38(SmC*) 8(SmA*)
LAHS3 (Host2+Dop2)	Cr <20 SmC* 59.8 N* 69.7 I	>49.7(Meso) >39.8(SmC*) 9.9(N*)
LAHS4 (Host1+Dop3)	Cr <20 SmC* 75.5 N* 92 I	>72(Meso) >55.5(SmC*) 16.5(N*)
LAHS5 (Host2+Dop3)	Cr <20 SmC* 60 SmA* 70 N* 72 I	>52(Meso) >40(SmC*) 10(SmA*) 2(N*)
LAHS6 (Host2+Dop1+Dop3)	Cr <20 SmC* 43 SmA* 73 I	>53(Meso) >23(SmC*) 30(SmA*)

§Cooling data. For crystallization temperatures of the mixtures please see text.

In all the mixtures either ferroelectric SmC* phase is induced or enhanced and it extends below room temperature. In order to check the possibility of supercooling of SmC* phase, the mixtures were cooled down to -40^{0}C and then heated up in a custom built heater with accuracy of ±1^{0}C. In all the mixtures transitions to partially crystalline or glassy state took place near 5^{0}C or below. For example, in LAHS1 the melting point was found to be 6^{0}C



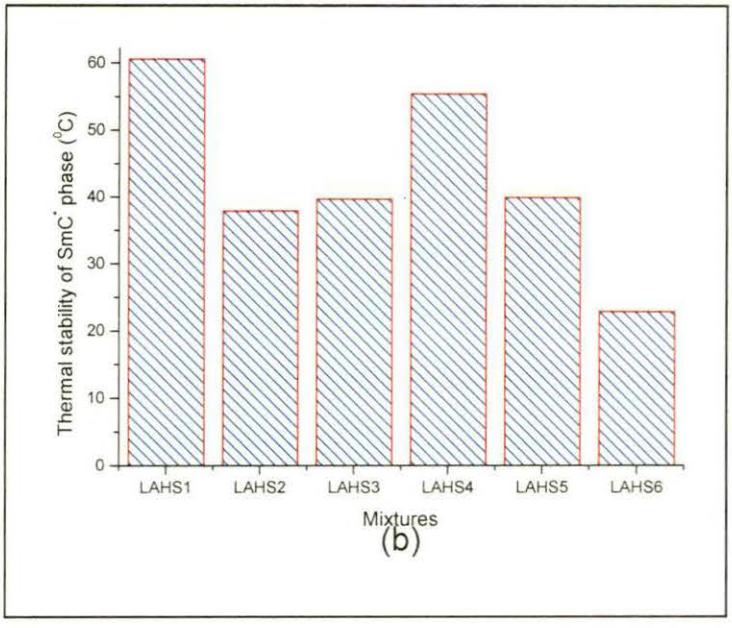


Figure 6.2.3. *Overall mesophase thermal stability (**a**) and thermal stability of SmC* phase (**b**) in the mixtures.*

while it partially crystallized below 5^0C. For LAHS3 these temperatures were -2 and -4^0C respectively.Overall mesophase stability and the stability of the SmC* phase are shown in **Figure 6.2.3.** Stability temperatures were estimated considering the lowest temperature of SmC* phase as 20^0C up to which dielectric studies were made in the mixtures. Mesophase

stability is found to be at maximum (>72^{0}C) in mixture LAHS4 followed by LAHS1 but the stability of the SmC* phase is maximum (60.6^{0}C) in LAHS1 followed by LAHS4. This is influenced by the broader stability of Host1. Other mixtures have similar overall mesophase stability although considerably less than the previous ones. Stability of SmC* phase in LAHS6 is very less compared to LAHS1, other mixtures have similar SmC* phase stability although considerably less than that of LAHS1, and LAHS4. If we compare the characteristics of the phase behaviour of different mixtures we observe the following:

- ❖ Ferroelectric SmC* phase is induced over a wide temperature range when a non-mesogenic chiral compound is used as a dopant in two different hosts with tilted SmC phase. As expected, chirality of the dopant, not mesogeneity, is the key factor for induction of ferroelectric behaviour in a tilted smectic host (LAHS1, and LAHS2). However, a considerable enhancement of SmC* phase is observed when a singly fluorinated compound possessing SmC* phase with chiral centers at one or both ends is used as dopant (LAHS3, LAHS4, and LAHS5).
- ❖ It is interesting to note further that dopants with same core structure but having chirality at one or both ends have similar effect on induction and thermal stability of SmC* phase (LAHS3, and LAHS5).
- ❖ Presence of the two dopants (DOP1 and DOP2) with chirality at both ends reduces the thermal stability of SmC* phase drastically and increases thermal stability of smectic A* (SmA*) phase similarly (LAHS2, and LAHS6).

From X-ray SAXS and WAXS study the temperature variations of average intermolecular distance (D) and layer spacing (d) in the ferroelectric SmC* phase were determined [353]. Results of only two mixtures, LAHS2 and LAHS5, have been presented here. Variations of average intermolecular distance (D) with temperature are shown in **Figure 6.2.4.** Mixtures of DOP1 in Host2 (LAHS2) show slightly increasing trend in D with temperature. On the other hand, LAHS5 which is mixtures of DOP3 in Host2 shows slightly decreasing trend. Temperature variations of layer spacing (d) in SmC* phase are shown in **Figure 6.2.5.** Layer spacings are found to differ marginally among the mixtures. This is expected behaviour since the weighted average length of the molecules in the mixtures varies from 30.3 to 31.1 Å. In mixture LAHS2 it shows slightly decreasing trend and in LAHS5 it remains almost constant.

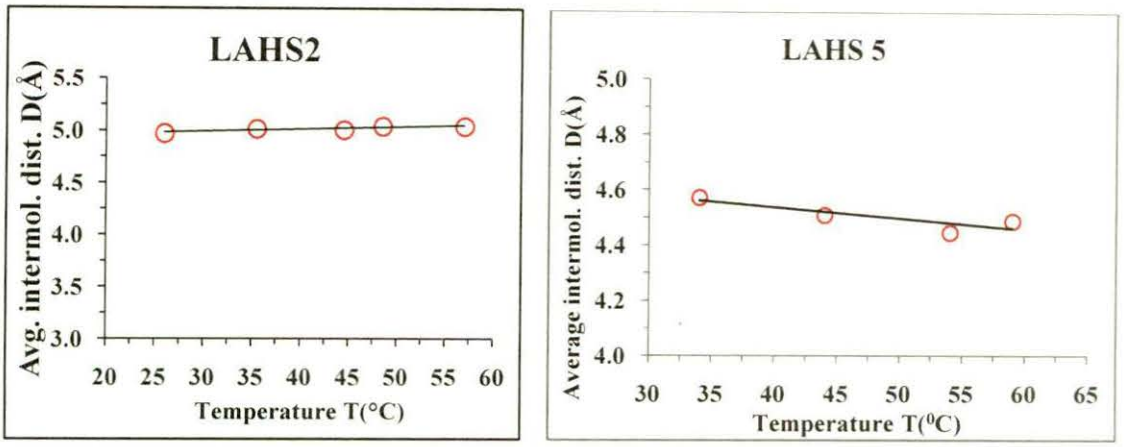


Figure 6.2.4. Variations of average intermolecular distance (D) with temperature

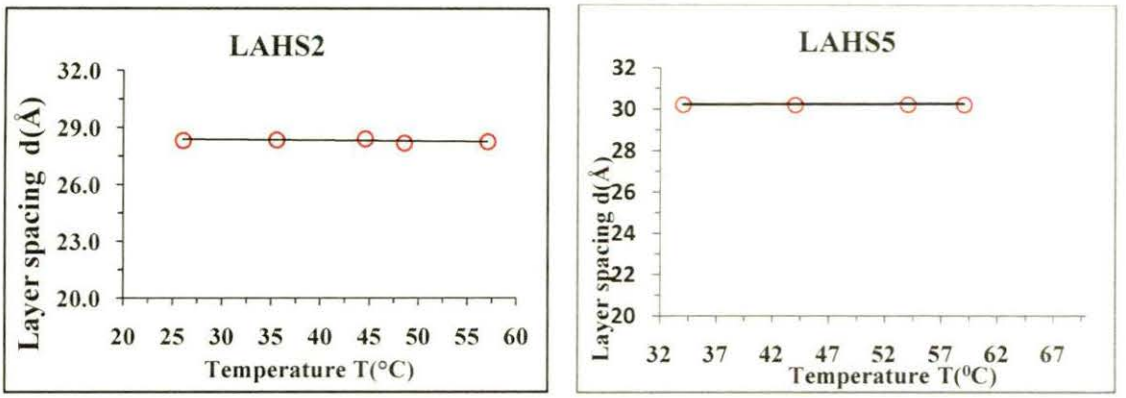


Figure 6.2.5. Temperature variations of layer spacings (d) in the ferroelectric phase

Table 6.2.2
Spontaneous polarization of the mixtures at room temperature (20°C).

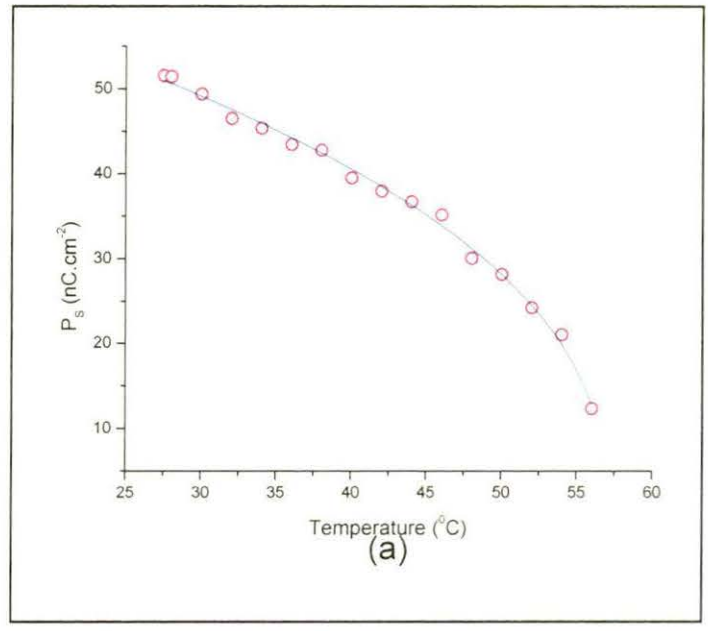
Mixture	LAHS 1	LAHS 2	LAHS 3	LAHS 4	LAHS 5	LAHS 6
P_S(nC/cm^2)	58.0	52.4	18.2	62.2	44.9	12.9

Values of spontaneous polarization (P_S) of the mixtures are found to vary widely (12.9 - 62.2 nC/cm^2) at room temperature (**Table 6.2.2**). We have also studied temperature variation of P_S and these are shown for mixtures LAHS2 and LAHS5 in **Figure 6.2.6**. According to the mean-field model P_S should obey the relation $P_S = P_0(T_C - T)^{\beta}$, where T_C is the SmC*- SmA* transition temperature [354]. Measured data fitted nicely to above equation with $T_C = 58.2 \pm 0.02^0$C and β=0.42±0.03 for LAHS2 and $T_C = 53.7 \pm 0.8^0$C and β=0.43±0.05 for LAHS5. Since fitted β values deviate from the mean field value (0.5), the SmC*- SmA* transition may

not be strictly second order in nature. Comparing P_S values of the mixtures it may be inferred that

- Mixtures may be grouped into three major categories: relatively high P_S (mixtures LAHS 1, 2, 4, and 5), medium P_S (LAHS3) and low P_S (LAHS6). Mixtures with dopants having chiral centres at both ends give rise to high P_S, mixture with dopant having one chiral centre results in medium P_S and mixture simultaneously containing the above two dopants results in low P_S. Hence the spontaneous polarization value for LAHS 6 is the smallest probably because of the compensation of polarization between two chiral compounds having opposite optical rotations.
- When a dopant having singly fluorinated chiral groups at one end is replaced by a dopant with similar chirality at both ends, P_S increases by about 2.5 times (LAHS3 to LAHS5), although their effect on induction and thermal stability of SmC* phase is similar.
- Polarization values of mixtures LAHS3, LAHS5, and LAHS6 are within acceptable limits for various applications [349].

Thus by choosing appropriate chiral dopant one can get optimum Ps value to get desired level of switching time as discussed in chapter 2 and 5.



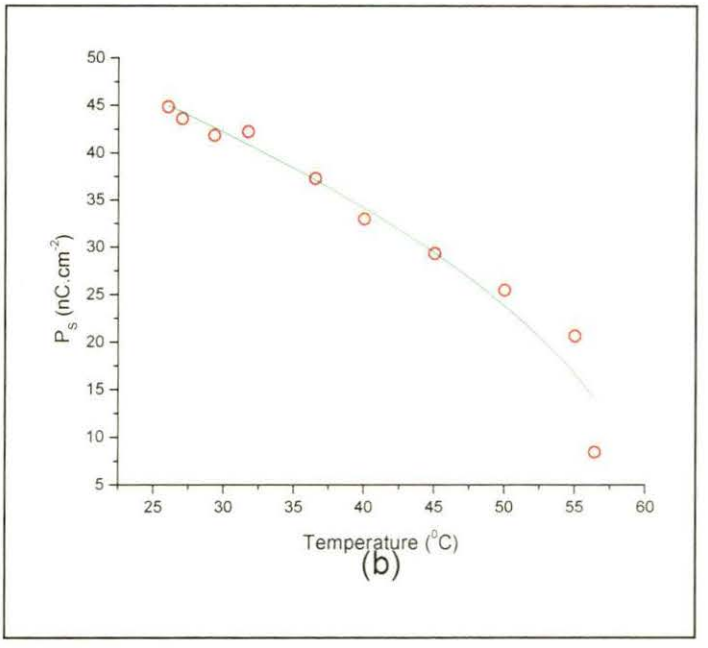
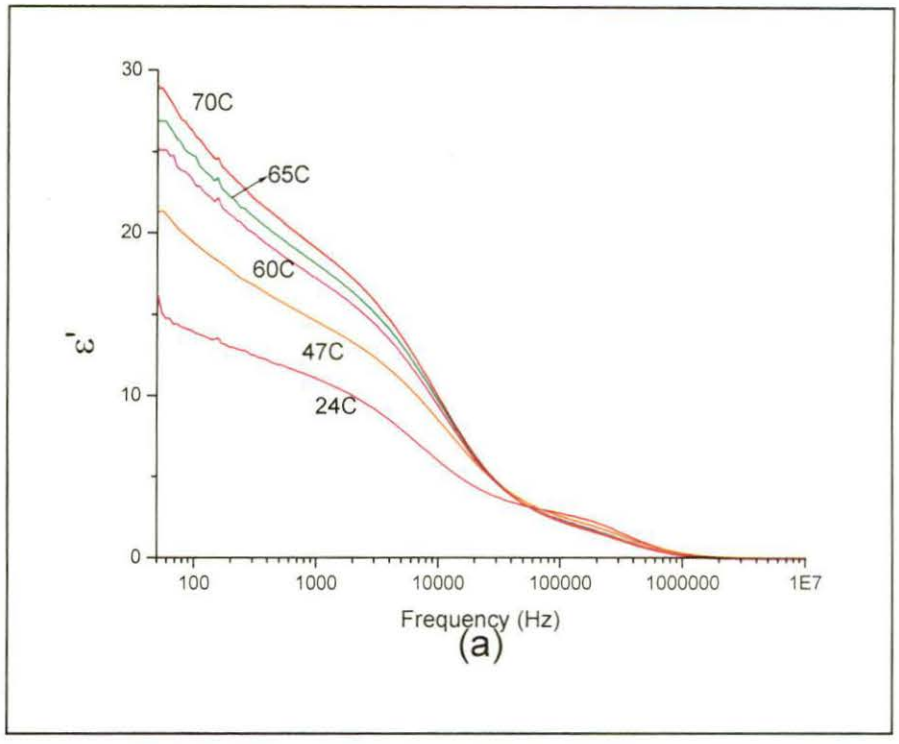


Figure 6.2.6. *Temperature variation of P_S in LAHS2 (a) and LAHS5 (b). Mean-field model fitted curve is also shown*

Tilt angle (θ) was also measured by electro-optic method in mixtures LAHS2 and LAHS6 and found to be 24^0 and 18^0 respectively. From X-ray study tilt angle of the mixtures were found to be 21.9^0, 22.2^0, 16.8^0, 16.9^0, 10.0^0 and 18.2^0 respectively in mixtures LAHS1 to LAHS6 [353]. It is observed that replacement of 50% of terphenyl dopant with chirality at both ends by singly fluorinated phenyl pyrimidene dopant also with chirality at both ends (LAHS2→LAHS6) reduces the tilt angle considerably. Reduced tilt angle is desirable for fast switching of FLC devices as discussed in chapter 2 and 5.

Though all the prepared mixtures exhibit ferroelectric SmC* phase, different types of dielectric responses were observed in frequency domain dielectric spectroscopy study. In SmC* phase, dielectric increment ($\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$) increases with temperature in mixture LAHS1 while it decreases in mixtures LAHS2 and LAHS3. In the remaining mixtures (LAHS4 to LAHS6) it first increases then decreases with temperature. As expected, in paraelectric SmA* phases, $\Delta\varepsilon$ falls from those in ferroelctric SmC* phases. Exemplary absorption and dispersion curves for two mixtures are shown in **Figures 6.2.7** and **6.2.8**.



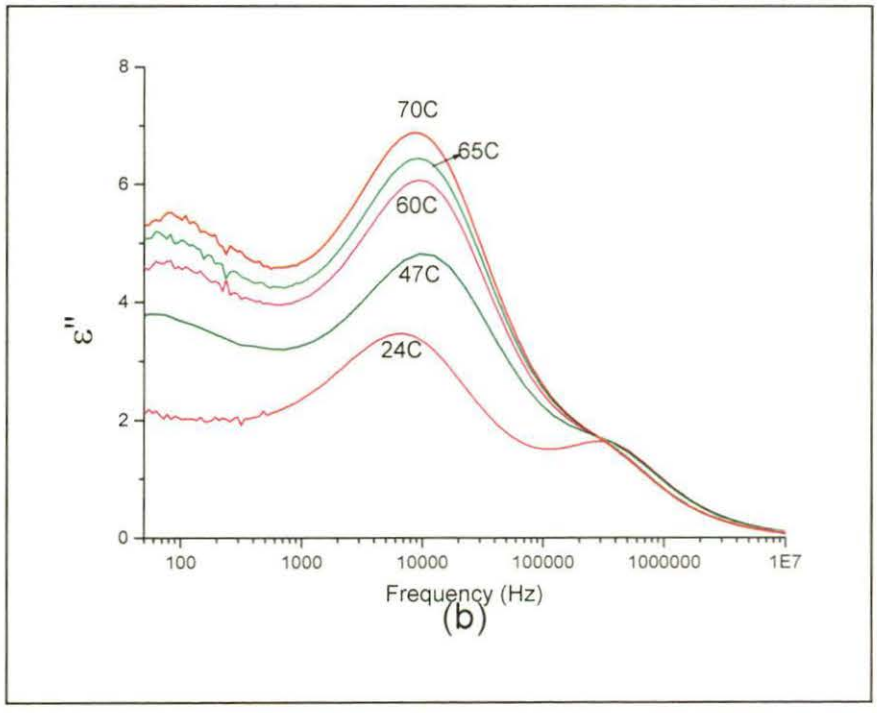
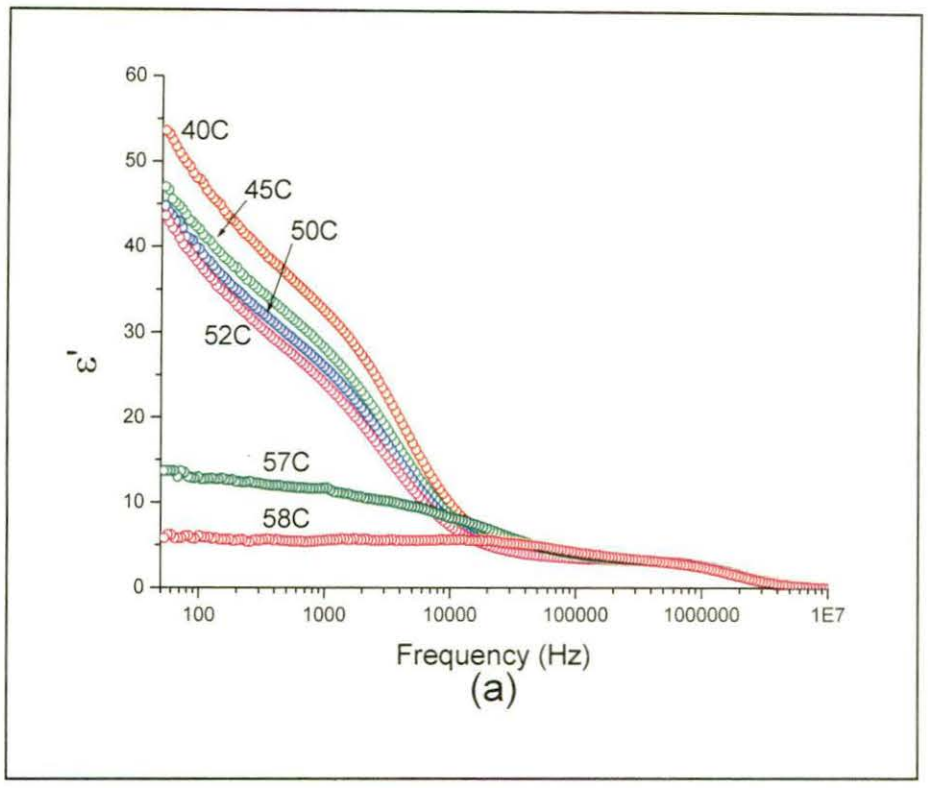


Figure 6.2. 7. *Real (**a**) and imaginary (**b**) parts of dielectric constants as a function of frequency at different temperatures for LAHS1.*



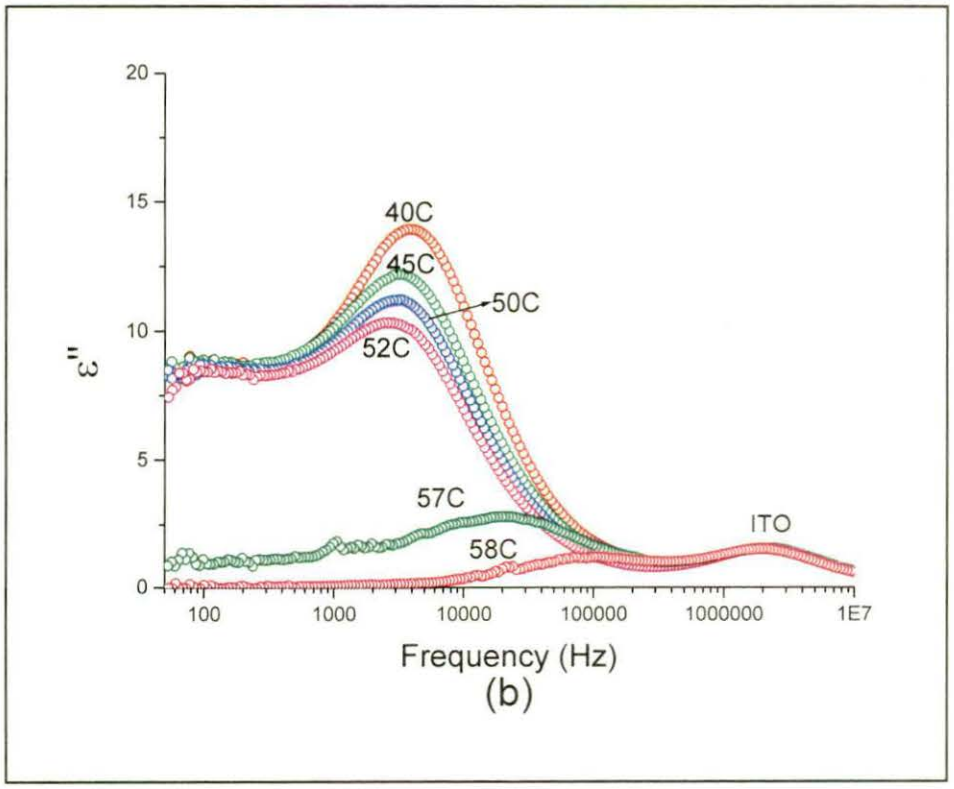


Figure6.2. 8. *Real (a) and imaginary (b) parts of dielectric constants as a function of frequency at different temperatures for LAHS2.*

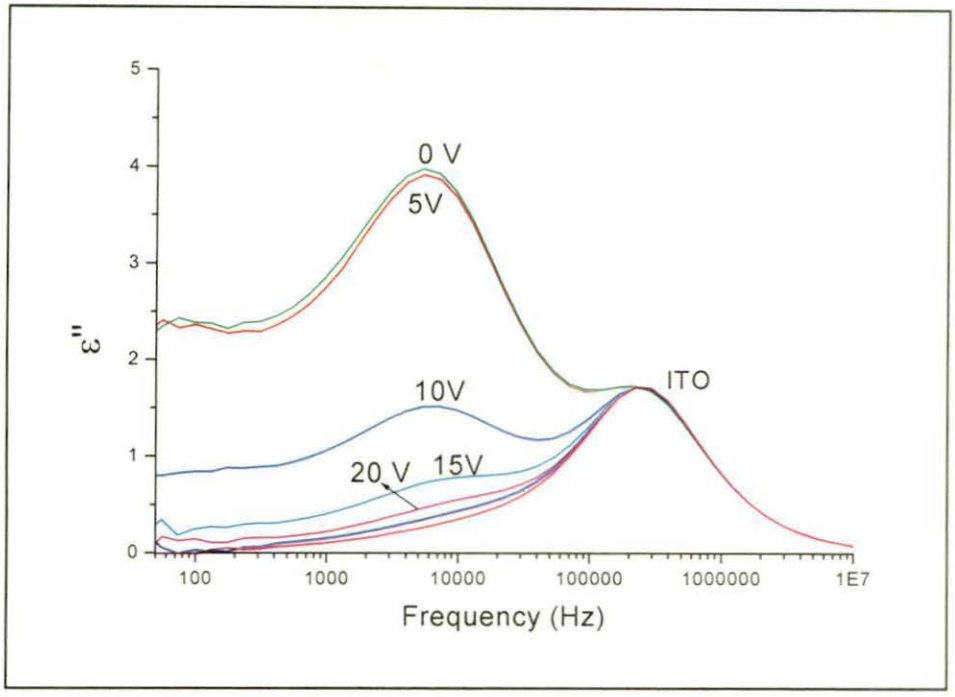


Figure 10.2.9. *Bias dependent dielectric spectra of LAHS1 at 22^{0}C.*

Table 6.2. 3
Critical frequencies of the *Goldstone mode* in the mixtures at room temperature

Mixture	LAHS 1	LAHS 2	LAHS 3	LAHS 4	LAHS 5	LAHS 6
Critical freq.(kHz)	6.5	4.1	1.4	10.6	9.5	0.7

In the observed frequency range and in planar orientation geometry, only collective mode relaxation behavior of the mixtures could be studied [159]. As noted earlier Goldstone mode arises due to collective fluctuations in the azimuthal orientation of the molecular directors and *soft mode* relaxation behaviour appears in the dielectric spectrum due to the collective fluctuations in the tilt angles of the molecules. *Goldstone mode* (GM) relaxation processes are observed in all the present mixtures in SmC* phase as shown in **Figures 6.2.7** and **6.2.8** for two mixtures. The critical frequencies ranges from 10.6 kHz in LAHS4 to 0.7 kHz in LAHS6 (**Table 6.2.3**) and found to have small temperature dependence as expected from generalized Landau theory. Critical GM frequencies are large in some mixtures compared to the values usually observed in SmC* phases of pure FLC compounds. *Soft mode* (SM) processes are also exhibited by mixtures LAHS2, LAHS5, and LAHS6. Mixtures LAHS1, and LAHS4 show another relaxation process at frequencies lower than GM frequencies which might be a *surface mode* [355]. Mixture LAHS3 shows only GM process.

GM processes can be suppressed by applying various bias voltages: 20 V in LAHS1, LAHS2, and LAHS4; 15 V was sufficient in LAHS6, 10 V in LAHS3 whereas 5 V was sufficient in LAHS5. Bias dependent spectra for LAHS1 are shown in **Figure 6.2.9** as a representative case.

A close look into the absorption behaviour of the mixtures reveals that mixture LAHS3 having dopant with chirality only at one end in a host containing shorter rigid core molecules exhibits only GM while mixtures having dopant with chirality at both ends in the same host exhibit both GM, and SM (LAHS2, LAHS5, LAHS6). On the other hand, mixtures having dopant with chirality at both ends but in a host containing longer rigid core molecules exhibit GM and *Surface modes* (LAHS1, LAHS4).

Critical frequency of the *Goldstone mode* is found to be highest (10.6 kHz) in LAHS4 containing long rigid core structured molecule in host mixture (Host 1) and singly fluorinated molecule with chirality at both ends as dopant (DOP3). Next highest critical frequency (9.5 kHz) is observed in LAHS5 where molecules with less rigid core structure are used in host mixture (Host 2), the dopant remaining same. However, when a non-fluorinated molecule but with chirality at both ends is used (DOP1) in Host 1, critical frequency reduces to 6.5 kHz (LAHS1), which is 4.1 kHz less than that of LAHS4.

In mixture LAHS2 – containing molecules with less rigid core structure in host mixture (Host 2) and a doubly chiral non-fluorinated dopant (DOP1), critical frequency is reduced further to 4.1 kHz. In mixture LAHS3 where a singly chiral fluorinated molecule is used as dopant (DOP2) in Host 2, critical frequency reduced considerably to 1.4 kHz. Dopant of mixture of fluorinated and non-fluorinated molecules with chirality at both ends in Host 2 resulted in the least critical frequency of 0.7 kHz in mixture LAHS6. Thus it may be concluded that rigidity of the core structure, nature of chirality and extent of fluorination of the constituent molecules have pronounced effect on the collective mode relaxation behaviour of the mixtures.

6.4. CONCLUSION

Six multi-component room-temperature FLC mixtures have been formulated using two different types of host mixtures and three different types of dopants. Phase behaviour of the mixtures is investigated using optical polarizing microscopy, dielectric spectroscopy and electro-optic methods. In all the mixtures SmC* phase is either induced or enhanced. Effect of host molecules and various dopants on the occurrence and thermal stability of different phases has been discussed. Chirality of the dopant is found, as expected, to be the key factor for

induction of ferroelectric behaviour in a tilted smectic system. On the other hand, a considerable enhancement of SmC* phase is observed when a singly fluorinated compound possessing **SmC*** phase with chiral centers at one or both ends is used as dopant.

Values of spontaneous polarization are found to vary between 13-62 nC/cm^2 at room temperature. It is observed that mixtures with dopants having chiral centres at both ends posses relatively high P_S compared to mixtures with dopant having one chiral centre. Mixture with two chiral compounds having opposite optical rotations is found to have minimum spontaneous polarization. Minimum X-ray tilt (θ) is observed in mixture LAHS5. Thus optimum value of switching time in mixture can be obtained by choosing proper host and chiral dopant thereby controlling θ and P_S.

Different types of dielectric absorption behaviour were observed in planar geometry of the FLC cells. Critical frequencies of GM are found to vary widely in the mixtures - from 10.6 kHz to 0.7 kHz. Rigidity of the core structure, nature of chirality and extent of fluorination of the constituent molecules are found to have pronounced effect on the collective mode relaxation behaviour of the mixtures.