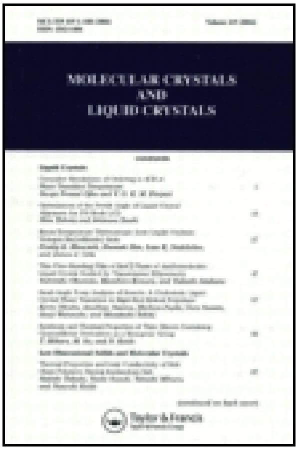


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

DIELECTRIC RELAXATION MODES IN FERROELECTRIC LIQUID CRYSTAL MIXTURES

Jasjit K. Ahuja [a] , Arvind K. Gathania [a] & K. K. Raina [a]

[a] School Of Basic Applied Sciences, Thapar Institute of Engineering and Technology, Patiala, 147 004, (India)

To cite this article: Jasjit K. Ahuja, Arvind K. Gathania & K. K. Raina (2001): DIELECTRIC RELAXATION MODES IN FERROELECTRIC LIQUID CRYSTAL MIXTURES, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 271-281

To link to this article: http://dx.doi.org/10.1080/10587250108023970

Mol. Cryst. and Liq. Cryst., 2001, Vol. 366, pp. 271-281
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Dielectric Relaxation Modes in Ferroelectric Liquid Crystal Mixtures

JASJIT K. AHUJA, ARVIND K. GATHANIA and K.K. RAINA*

School Of Basic Applied Sciences, Thapar Institute of Engineering and Technology, Patiala – 147 004 (India)

Dielectric measurements in the frequency range 50 Hz to 1 MHz at varying bias and temperatures have been carried out in three ferroelectric liquid crystal mixtures in the SmC* and SmA phases aligned in planar orientation. The sample cells are in volume stabilized and surface stabilized geometry. Here we report the observation of relaxation modes namely New Relaxation Mode *"NRM"*, Surface Stabilized Domain Mode *"SSDM"* and Bulk Domain Mode *"BDM"*. The relaxation frequency f_r and dielectric strength $\Delta\varepsilon$ corresponding to these modes has been evaluated.

Keywords: Dielectric Relaxation; Goldstone Mode; Soft Mode; Domain Mode; New Relaxation Mode

I. INTRODUCTION

Dielectric spectroscopy studies on ferroelectric liquid crystals (FLCs) gives useful information about the static and dynamic properties of these systems [1-2]. The well-known relaxation modes in FLCs are Goldstone mode "*GM*", Soft Mode "*SM*" and the Polarization mode *"PM"* (usually

---

* Author for correspondence. E-mail: raina@tietp.ren.nic.in

appears at very high frequencies >500MHz). These modes occur due to the fluctuations of the order parameter and the molecular rotation around long axis of the molecule [3-4]. The *GM* appears in the SmC* phase due to the fluctuations of the azimuthal angle and has a characteristic frequency <10kHz. The *SM* appears near SmC* - SmA phase transition temperature (T_{C*A}) due to the tilt angle fluctuations as near T_{C*A} the system becomes soft against these fluctuations. This mechanism is usually observed >10kHz with a strong temperature dependence [5-7].

In this paper, we shall present the experimental results of dielectric relaxation modes studied in three different FLC mixtures as a function of field frequency, temperature and the bias field. We report the appearance of New Relaxation Mode *"NRM"*, Bulk Domain Mode *"BDM"* and the Surface Stabilized Domain Mode *"SSDM"* in addition to *GM* and *SM*. The effects of surface interactions on dielectric properties have also been discussed.

II. THEORETICAL BACKGROUND

It is known that due to the presence of chirality in SmC* phase the in-plane polarization perpendicular to the direction of the tilt is given by $\mathbf{P} = \mathbf{P}_X X + \mathbf{P}_Y Y$. The order parameter ($\xi$) and the polarization (P) can be written as:

$$\xi_1 = \theta_0 \cos(qZ) \qquad \xi_2 = \theta_0 \sin(qZ) \qquad \text{-----(1)}$$

$$P_X = -P_0 \sin(qZ) \qquad P_Y = P_0 \cos(qz) \qquad \text{-----(2)}$$

Where Z is the co-ordinate axis normal to smectic layer plane, $q = 2\pi/p_0$ is the wave-vector of helical pitch (p_0). θ_0 and P_0 are the molecular tilt angle and spontaneous polarization respectively [3-4].

In the absence of an external dc bias, *GM* appears in the low frequency region (<10 kHz) whereas in the high frequency (>10 kHz) region *SM* is observable near $T_C{}^*{}_A$. The dielectric response in terms of dielectric susceptibility of these two modes is related to the dielectric strength as $\chi = \varepsilon_a \Delta\varepsilon$; where ε_a is the absolute permittivity of free space and $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$, ε_0 and ε_∞ are the static and infinite frequency dielectric constants respectively.

The external dc bias applied to the sample disturbs the helix in two ways. Firstly, in weak fields, the helix is disturbed due to the linear coupling between polarization (**P**) and the electric field (**E**). The net induced polarization thus increases. The dielectric response in that case will be $\chi = \chi_{GM} + \chi_{SM}$, where χ_{GM} and χ_{SM} are the dielectric susceptibility of *GM* and *SM* respectively. Here *GM* appears with suppressed dielectric response. The dielectric response χ is given as

$$\chi = lt_{E\to 0} \frac{<P_i>}{E} \qquad \text{----(3)}$$

where $\mathbf{P}_i$ is the average induced polarizations and **E** is the magnitude of the applied static electric permittivity [3-4, 8-9].

Secondly, we believe that in presence of both strong dc and ac field, the coupling between **P** and **E** becomes so strong that the helical texture breaks up into the modulated domain structures. It reduces the electro-static energy. The dielectric response to the susceptibility would then be come $\chi = \chi_{DM} + \chi_{SM}$, χ_{DM} and χ_{SM} are the Domain Mode "*DM*" and *SM* susceptibilities respectively [3-9].

III. EXPERIMENTAL

The frequency and temperature dependence of the complex dielectric permittivity has been studied in three novel ferroelectric liquid crystal mixtures namely FLC-6430, SCE-13 and FLC-6980. Their phase transition temperature, helical pitch p_0 and tilt angle θ values are given in Table 1.

TABLE I: Phase transition temperature and the material parameters of the mixtures studied

MATERIAL PARAMETERS	**LC-I FLC-6430**	**LC-II SCE-13**	**LC-III FLC-6980**
SmC* - SmA	57^0	61^0	64^0
SmA – N*	-	91^0	76^0
N* - Isotropic	-	115^0	81^0
SmA – Isotropic	65^0	-	-
Helical Pitch p_0	0.43μm	10-12μm	10-12μm
Tilt angle θ	27^0	20.5^0	22^0
Spontaneous Polarization P_S	85^0	37^0	12^0

In order to study dielectric relaxation mechanisms, the mixtures were sandwiched in 5μm thin cells between two ITO coated glass substrates. The substrates were pre-treated with polyimide coating (parallel rubbing direction). The liquid crystal mixture was filled in these cells by the capillary action above isotropic temperature of the samples and then cooled at 0.1^0C/min. in presence of an ac electric field (~10Hz and $10V_{PP}$) in a LINKAM temperature programmer cum hot stage (model TP90 and THS-600). The optical textures of different liquid crystalline phases were observed through GETNER polarizing microscope. The complex permittivity was measured using Hewlett-Packard Impedance

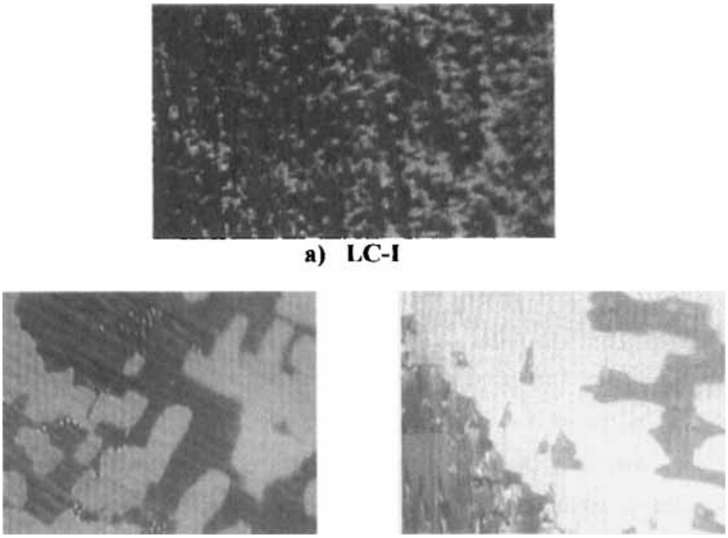
Analyzer (model HP4192A) in the frequency range 50Hz to 1MHz at different temperatures and dc bias upto 2.0V/μm. The effects of bias field and temperature on various relaxation modes was then investigated. The detailed measurement technique is given elsewhere [10].

IV. RESULTS AND DISCUSSION

IV.1 Microscopic Studies

We considered three mixtures LC-I, LC-II and LC-III. As in LC-I the $d_S << p_0$ i.e. the surface forces are weak enough to suppress the helix but strong enough to generate the bookshelf geometry. We consider LC-I in the volume stabilized ferroelectric liquid crystal (VSFLC) state, while LC-II and LC-III ($p_0 >> d_S$) are considered in the surface stabilized ferroelectric liquid crystal (SSFLC) geometry. In the SSFLC geometry, the bounding plates suppress helix and the surface interactions are strong enough to unwind it. Application of an alternating electric field E perpendicular to the helix axis gives two bistable states with opposite polarization +P and –P [11].

Plate 1 (a) shows the optical texture of LC-I under the crossed polarizers at room temperature, while the textures of LC-II and LC-III confined in SSFLC geometry are shown in Plates 1(b) and 1(c). The sample of LC-I is considered in VSFLC whereas LC-II and LC-III are considered in SSFLC configuration. The ferroelectric domains +P and –P are clearly visible in SSFLC cells with comparable brightness. The domains are separated by walls, which show up dark regions because in going from +P to –P, the director $\hat{n}$ rotates through an extinction angle with chevron texture.



a) LC-I

b) LC-II **c) LC-III**

Plate 1: Microscopic texture of **a)** LC-I **b)** LC-II **c)** LC-III under crossed polarizers at room temperature in absence of an external dc bias. See Color Plate IX at the back of this issue.

IV.2 Dielectric Relaxations

Effects of frequency

The relaxation modes observed in three FLC mixtures are shown in Figure 1 in the form of Cole-Cole plot. We notice that LC-I shows large dispersion as compared to LC-II and LC-III due to the higher values of P_S. In LC-I, *GM* appears due to the phase fluctuations of azimuthal angle while in LC-II and LC-III the *GM* is probably caused by anchoring at both the substrate surfaces and the chevron interface. Figure 1-[Inset] shows the high frequency relaxation mode defined as *NRM*. We believe that it has resulted from the tiny surface domains, which contribute to the helix unwinding due to the pinning effects [11-13].

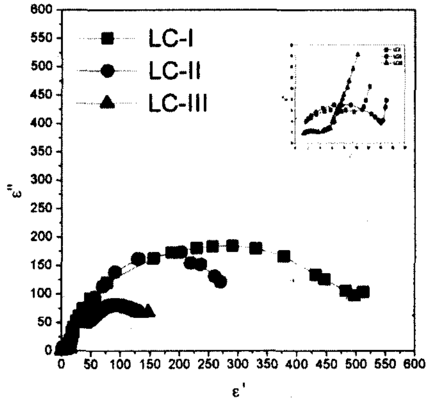


Figure 1: Cole-Cole plot of *GM* and *NRM* in VSFLC (LC-I) and SSFLC (LC-II, LC-III) cells at 35^{0}C in the absence if an external dc bias. Inset: appearance of *NRM* in three FLC mixtures.

Effects of temperature

It is observed from Figure 2(a,b) that with the increase of temperature the relaxation frequency as well as the dielectric strength of the *GM* remains almost constant whereas near T_{C*A} *SM* starts appearing. It obeys the Curie-Weiss law. The f_{rGM} gives the measure of the switching time of the electro-optic cells. The temperature dependence of f_{NRM} is shown in Figure 3.

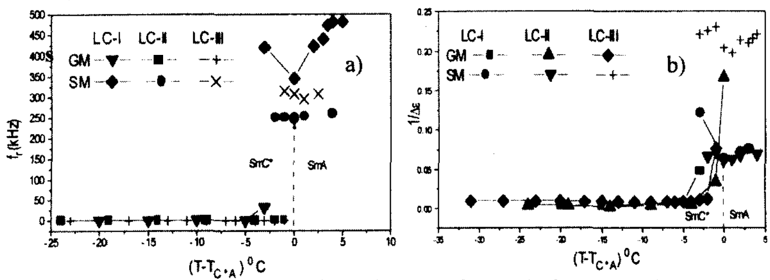


Figure 2: Temperature dependence of **a)** Relaxation frequency **b)** Dielectric strength of *GM* and *SM* in VSFLC (LC-I) and (LC-II, LC-III) cells in the absence of an external dc bias.

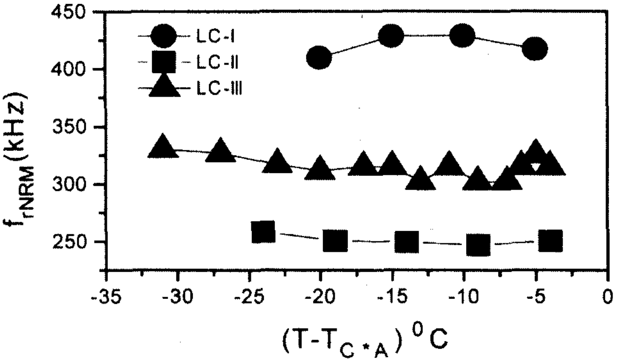


Figure 3: Temperature dependence of the relaxation frequency of *NRM* in the absence of an external dc bias.

Effects of external bias

The effects of external bias on the ferroelectric liquid crystals gives rise to several interesting relaxation processes. It was observed that in all the three FLC mixtures, the dielectric increment decreases with increase of dc field due to the suppression of helix. It suppresses the *GM* but still there can be a residual part of *GM*, which could not be suppressed completely. We define the residual part of *GM* as Domain Mode *"DM"*. We believe that it appears due to the formation of the modulated domains with different periodicities in the layers in presence of electric field. The formation of the different periodicities is connected with the distribution of the density of charge carriers within the layers. In addition, at this stage the coupling between P and E becomes so strong that the helical structure could break up into the modulated domains to reduce the electrostatic energy. The length of domain period l_D depends upon the value of spontaneous polarization ($l_D \sim P_S^{-2}$) [11].

Figure 4 shows the bias dependence of the f_{rGM} and f_{rNRM} at room temperature. It is seen that f_{rGM} increases with the increase of bias and then its value rises abruptly. This abrupt rise in relaxation frequency perhaps hints at the appearance of *DM*. In VSFLC cell configuration, we call it a Bulk Domain Mode *"BDM"* which occurs due to the modulated domains in the bulk sample. On the other hand in SSFLC cells, the mode could be surface stabilized domain mode *"SSDM"*. It is seen from Figure 4 that with the increase of bias the f_{rNRM} in VSFLC increases with bias and then saturates beyond 1.0V/μm. It could be due to the strong coupling of surface domains with the external electric field and the ionic contribution of the multi-component mixture.

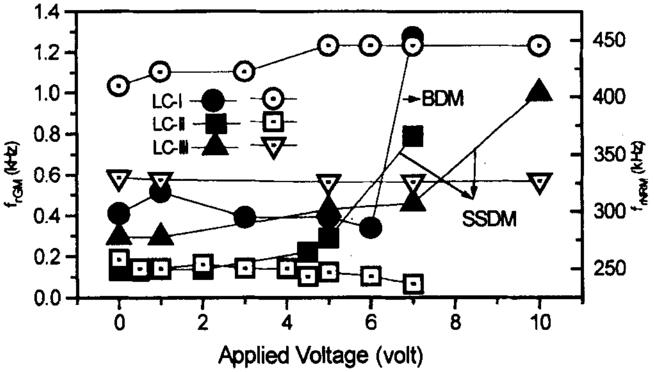


Figure 4: Bias voltage dependence of the relaxation frequency of *GM, NRM, BDM, SSDM* for VSFLC (LC-I) and SSFLC (LC-II, LC-III) cells at room temperature. Solid symbols represent the f_{rGM} while hollow symbols represent f_{rNRM}.

The dielectric parameters of the various relaxation modes in three different FLC mixtures studied in our experiment are given in Table 2.

Table 2: Material Parameters of LC-I, LC-II and LC-III Mixtures

Material Parameters	**FLC-6430 (LC-I)**	**SCE-13 (LC-II)**	**FLC-6980 (LC-III)**
•• f_{rGM} (kHz)	0.44	0.129	0.17
•• $\Delta\varepsilon_{GM}$	525.0	309.0	106.0
•• f_{rNRM} (kHz)	409.6	258.0	330.0
•• $\Delta\varepsilon_{NRM}$	12.95	16.0	17.0
$^{\#}f_{rBDM}$ / f_{rSSDM} (kHz) at 1.4V/μm	1.3	0.79	1.0 at 2.0V/μm
$^{\#}\Delta\varepsilon_{BDM}$ / $\Delta\varepsilon_{SSDM}$ at 1.4V/μm	9.3	4.37	4.5 at 2.0V/μm
$^{\#\#}f_{rSM}$ (kHz) at T_{C^*A}	345.7	248.3	298.86
$^{\#\#}\Delta\varepsilon_{SM}$ at T_{C^*A}	16.0	16.5	4.89

- •• Measurements taken at 35^0C, 0.0V/μm
- $^{\#}$ Measurements taken at 35^0C
- $^{\#\#}$Measurements taken at 0.0V/μm

CONCLUSIONS

- Dielectric Relaxation studies have been carried out in three FLC mixtures differentiated on the basis of their P_S values and the helical pitch. We considered LC-I mixture in the VSFLC geometry ($d_S >> p_0$), while LC-II and LC-III have been considered in the SSFLC geometry ($d_S << p_0$). Five relaxation modes have been noticed.
- *GM* appears in the SmC* phase in the absence of an external dc bias.
- *NRM* appears in all the three FLC mixtures above 100kHz due to the surface anchoring effects. *NRM* relaxation frequency increases with bias in VSFLC perhaps due to the strong coupling of surface domains at higher bias while it remains nearly constant with bias in SSFLC cell configuration. It indicates strong surface anchoring energy in SSFLC as compared to VSFLC.

- *BDM* appears in LC-I due to the formation of the modulated domains in bulk while *SSDM* appears in LC-II and LC-III due to the formation of the modulated domains in the bookshelf interface. Both these modes are the residual parts of *GM* and appear due the suppression of *GM* in presence of an external dc bias.

ACKNOWLEDGEMENTS

We are grateful to Dr. M.Schadt (Hoffmann-La-Roche, Switzerland) for providing LC-I and LC-III mixtures and to BDH, UK for providing LC-II mixture. The interest of Professor M.P. Kapoor, Director TIET in these studies is gratefully acknowledged. This work is supported by DST, India vide grant no. SP/S2/M-49/97.

References

[1] L.A. Beresnev, L.M. Blinov, M.A. Osipov and S.A. Pikin, Mol. Cryst. Liq. Cryst., **158A**, 1–150 (1988) – *References there in.*

[2] F. Gouda, G. Anderson, M. Matuszczyk, K. Skarp and S.T. Lagerwall, J. Appl. Phys., **67(1),** 180 (1990).

[3] A. Levstik, T. Carlsson, C. Fillipic, T. Levstik and B. Zeks, Phys. Rev. A, **35**, 3527 (1987).

[4] T. Carlsson and B. Zeks, Phys. Rev., **36**, 1484 (1984).

[5] A.M. Biradar, S. Wrobel, and W. Haase, Phys. Rev. A, **39**, 2693 (1989).

[6] S. Hiller, A.M. Biradar, S. Wrobel and W. Haase, Phys. Rev. E, **53**, 1 (1996).

[7] M. Marzec, W. Haase, E. Jakob, M. Pfeiffer, S. Wrobel and T. Geelhaar, Liquid Crystals, **14(6),** 1967 (1993).

[8] K.K. Raina and Jasjit K. Ahuja, Mol. Cryst. Liq. Cryst., 155, **325** (1998).

[9] K.K. Raina and Jasjit K. Ahuja, J. Phys.: Condensed Matter, UK - (Communicated – Nov. – 1999).

[10] Ph. D Thesis, TIET (2000).

[11] Jasjit K. Ahuja and K.K. Raina, Jap. J. of App. Phys., 7A, **39**(2000).

[12] K.K. Raina, A.K. Gathania and B. Singh, J. Phys. Cond. Matter (UK), 11, 7061 (1999).

[13] K.K. Raina, A.K. Gathania and B. Singh, Pramana; J. Phys., **52(4),** 443 (1999).

[14] A.K. Gathania, B. Singh and K.K. Raina, J. Phys. Cond. Matter (UK), **11**, 3813 (1999).

[15] K.K. Raina and Jasjit K. Ahuja, Mol. Cryst. Liq. Cryst., 125, **338**(2000).