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Observation of relaxation modes in room temperature ferroelectric liquid crystal mixtures

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Abstract. The dielectric measurements in SmC* and SmA phases of a room temperature ferroelectric liquid crystal mixture FLC-6980 in the cells of different thickness in planer alignment have been carried out in the frequency range 100 Hz to 1 MHz. A relaxation mode (called NRM) whose dielectric increment is less than the Goldstone mode has been observed in the SmC* phase. This mode appears due to the surface effect. Goldstone mode and the soft mode was observable in the vicinity of SmC* – SmA transition temperature (T_{C^*A}). The dielectric parameters of the Goldstone mode, new mode and the soft mode have been studied as a function of frequency and temperature. The calculated values for f_{NRM}, $\delta\epsilon^{\mathrm{NRM}}$ and distribution parameter α_{NRM} are found to be 325 kHz, 6 and 0.156 for 5μm thick planer cell at 37°C. It is seen that in the vicinity of the T_{C^*A}, soft mode obeys the Curie–Weiss law given by mean field theory. The results have been compared with materials of large spontaneous polarization.

Keywords. Ferroelectric liquid crystal; dielectric increment; relaxation mode; Goldstone mode; soft mode.

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1. Introduction

Ferroelectric properties in liquid crystals are found in tilted smectic C phase due to the presence of chiral molecules in these systems [1]. The chiral smectic C (SmC*) phase is a low symmetric one with C_2 symmetry element. It has a layered structure and is formed due to the modulated structure of the director while going from one layer to another successively along the layer normal. During this process, a helical stripe like texture appears in the sample. This helix can be unwound by the external ac or dc field [2–6].

The dielectric spectroscopy of SmC* liquid crystal gives useful information about the static and dynamic properties of these compounds [7–13]. Dielectric response mainly consists of four modes. Out of these four modes, two are due to the fluctuations of the polarization order parameter having relaxation frequencies of the order of 500 MHz [14]. Other two modes are connected to the director fluctuations known as Goldstone mode (GM) and soft mode (SM) [2]. The GM appears due to the fluctuations in the azimuthal orientation

of the director in SmC* phase whereas the SM is due to the fluctuations in the amplitude of the tilt angle and appears in the vicinity of SmC* – SmA transition temperature (T_{C^*A}).

With the precision in the dielectric measurement techniques, new relaxation processes have been reported. For example, recently in the SmC* phase, bulk domain mode and surface domain mode have been reported for the first time after the suppression of the GM by the application of bias voltage [15–16]. These results indicate that the dielectric parameters are strongly dependent on the external bias voltage. Wrobel *et al* [17] reported new relaxation process in a fluorinated type ferroelectric liquid crystal (FLC) mixture and showed that the dielectric spectrum comes from four modes in this mixture. Majumder *et al* [18] have reported the appearance of an unknown mode which they proposed to have appeared due to various defects in the cell.

In this paper, we present the dielectric spectroscopy results in a novel room temperature FLC mixture having large pitch ($\approx$ 10 – 15μm) and low spontaneous polarization (21.7nC/cm^2) [19]. A new relaxation mode has been observed in the SmC* phase at 37°C showing relaxation frequency $\approx$ 325 kHz. The dielectric parameters of this mode have been evaluated. Near the transition temperature, soft mode suppresses this new mode. The soft mode parameters obey the Curie–Wiess law near T_{C^*A} as is given by the mean field theory. These measurements have been carried out in the absence of an external bias so that inferences can be drawn on the unperturbed structure. The results have been compared with mixture FLC-6430 (short pitch and large polarization) and discussed. The polarization modes, which usually occur at higher frequencies (500 MHz) could not be studied due to the limitation in the experimental set-up.

2. Experimental

Dielectric properties have been studied in liquid crystalline mixtures FLC-6980 and FLC-6430 (obtained from Hoffmann La Roche, Switzerland). The phase sequence of these mixtures as observed by thermal polarizing microscopy and differential scanning calorimetery are given below:

1. FLC-6980

$$\text{Cryst} \xrightarrow{-20^\circ\text{C}} \text{SmC}^* \xrightarrow{64^\circ\text{C}} \text{SmA} \xrightarrow{76^\circ\text{C}} \text{N}^* \xrightarrow{81^\circ\text{C}} \text{isotropic}$$

2. FLC-6430

$$\text{Cryst} \xrightarrow{-11^\circ\text{C}} \text{SmC}^* \xrightarrow{55^\circ\text{C}} \text{SmA} \xrightarrow{61^\circ\text{C}} \text{isotropic}$$

The mixture 1 has large pitch ($\approx$ 10 – 15μm) and low spontaneous polarization (21.7nC/cm^2) whereas mixture 2 has short pitch ($\approx$ 0.45μm) and high P_S (91nC/cm^2). The cells of the thickness 5.0μm and 7.5μm consisting of conducting indium tin oxide (ITO) coated glass substrates and pre-treated with polyimide coating at the surfaces were filled by the liquid crystal mixtures at their isotropic phase and then cooled @0.5°C/min and aligned. These cells have been calibrated using air and benzene as standard references

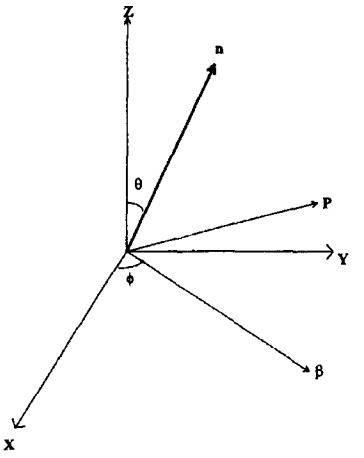


Figure 1. Local order and symmetry in the SmC* phase.

for calculating the absolute values of the dielectric permittivity. The dielectric measurements were then carried out in these sample cells aligned in a planer orientation. This alignment was confirmed when the texture was viewed through Getner microscope under crossed polarizers.

The sample cell was connected to Hewlett-Packard impedance analyzer model HP 4192A in the frequency range of 5 Hz to 13 MHz for obtaining the experimental results. The temperature of the sample was controlled and maintained at an accuracy of 0.1°C in Mettler temperature Programmer (FP 5) and hot stage (model FP 52).

3. Theoretical background

The structure of SmC* liquid crystal consists of a director ($\mathbf{n}$) tilted away from the layer normal ($\mathbf{z}$) by a constant tilt angle (θ_0) as shown in figure 1. Due to modulated structure the transverse spontaneous polarization ($\mathbf{P_S}$) normal to the tilt is locally induced. $\mathbf{P_S}$ changes its direction with helical structure and can be expressed as

$$\mathbf{P_S} \approx (\mathbf{z} \times \mathbf{n}). \tag{1}$$

The ordering of the molecules in the tilted phase is described by two order parameters, *i.e.* $\beta = (\beta_1, \beta_2)$ and $P = (P_x, P_y)$. β gives the direction and magnitude of the tilt. Both the order parameters are spacially modulated in the form of a helical structure given as

$$\beta(z) = \theta_0[\hat{x}\cos(qz) + \hat{y}\sin(qz)] \tag{2}$$

$$P(z) = P_0[-\hat{x}\sin(qz) + \hat{y}\cos(qz)], \tag{3}$$

where $\hat{x}$ and $\hat{y}$ are the respective unit vectors, θ_0 is the tilt angle of the molecules with layer normal, $q = 2\pi/L_0$, L_0 is the pitch of the helix. The director reorientation can be described

in terms of the real (ϵ') and imaginary (ϵ'') part of the complex dielectric permittivity (ϵ^*), which is given as

$$\epsilon^* = \epsilon' - i\epsilon'' \tag{4}$$

and

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0^{\mathrm{M}} - \epsilon_\infty^{\mathrm{M}}}{1 + (i\omega\tau_{\mathrm{M}})^{1-\alpha_{\mathrm{M}}}} + \frac{\epsilon_0^{\mathrm{SM}} - \epsilon_\infty^{\mathrm{SM}}}{1 + (i\omega\tau_{\mathrm{SM}})^{1-\alpha_{\mathrm{SM}}}} + \frac{\epsilon_0^{\mathrm{GM}} - \epsilon_\infty^{\mathrm{GM}}}{1 + (i\omega\tau_{\mathrm{GM}})^{1-\alpha_{\mathrm{GM}}}} + \frac{\epsilon_0^{\mathrm{NRM}} - \epsilon_\infty^{\mathrm{NRM}}}{1 + (i\omega\tau_{\mathrm{NRM}})^{1-\alpha_{\mathrm{NRM}}}}, \tag{5}$$

where ϵ_∞ is the high frequency limit of the dielectric permittivity, $\delta\epsilon^{\mathrm{M}}$, $\delta\epsilon^{\mathrm{SM}}$, $\delta\epsilon^{\mathrm{GM}}$, and $\delta\epsilon^{\mathrm{NRM}}$ represents dielectric increments (i.e., $\delta\epsilon^{\mathrm{i}} = \epsilon_0^{\mathrm{i}} - \epsilon_\infty^{\mathrm{i}}$, where i is M, SM, GM and NRM) of the molecular mode, the SM, GM and new relaxation mode respectively. τ_{M}, τ_{SM}, τ_{GM} and τ_{NRM} are relaxation times, whereas α_{M}, α_{SM}, α_{GM} and α_{NRM}, represent distribution parameters of these modes respectively. The second term in (5) is connected to the molecular reorientation around long molecular axes, third and fourth term represent the SM and GM respectively. The last term represents the contributions from the relaxation process which has been observed due to the formation of new mode.

4. Results and discussion

The variation of the complex permittivity (ϵ' and ϵ'') of FLC-6980 as a function of frequency and sample thickness at 37°C is shown in figure 2. It is interesting to note that in the low frequency region, the permittivity ϵ' decreases sharply. On the other hand, ϵ'' component initially increases in the frequency regime 0.1 kHz to 0.26 kHz and then decreases. Beyond 100 kHz, it increases further and attains a maxima at 297 kHz (for 7.5μm thick cell) and shows a dominant relaxation mode at this frequency. We call this as new relaxation mode (NRM). This mode has also been observed in cells of different

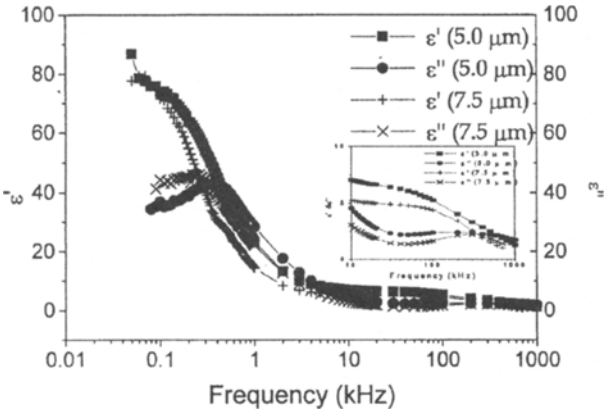


Figure 2. Frequency dependence of ϵ' and ϵ'' for 5μm and 7.5 μm cell thickness.

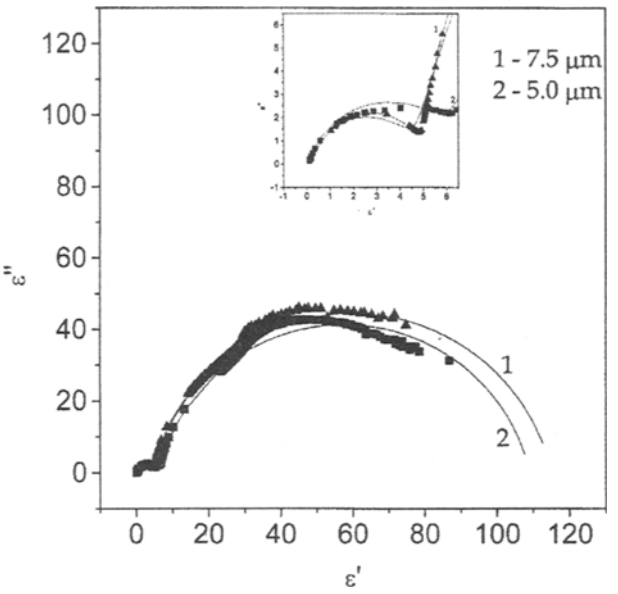


Figure 3. Cole–Cole plot of FLC-6980 sample at different cell thickness.

thickness [figure 2 inset]. Although some groups have reported the existence of other modes earlier [15–18, 20] but we believe that since GM has a dominant contribution in this temperature range, the new mode must have appeared due to surface effects and could have resulted from the surface domains due to surface pinning and domain walls which contribute to the helix unwinding. Thus the NRM can be considered as a consequence of surface effects. It is interesting to see this relaxation phenomena in the Cole–Cole plot as shown in figure 3. The smaller semi-circles in this figure represent the relaxation due to the NRM [figure 3, see inset] whereas, bigger semicircles represent the contribution due to GM and some minor contributions from NRM. The relaxation due to the collective mode has been observed at T_{C^*A} in the sample.

The typical temperature dependence of the inverse of dielectric increment for the NRM and SM for two FLC-mixtures is shown in figure 4(a). The inverse of dielectric increment for GM as a function of temperature is shown in figure 4(b) for FLC-6980 sample at different cell thickness. The results have been evaluated using (5). A comparison from the results obtained for two FLC-mixtures reveals that for the same sample thickness, the material with large spontaneous polarization (FLC-6430) shows higher dielectric increment corresponding to the NRM. It is interesting to note that the sample thickness also effect the dielectric increment of this mode. It is also seen that in the vicinity of the T_{C^*A}, SM dielectric parameters follow the Curie–Weiss law [17,21].

The relaxation frequency (f_i) of the ith modes can be evaluated using an expression [22]

$$\frac{v}{u} = (\omega\tau)^{1-\alpha}, \tag{6}$$

where

$$v = [(\epsilon_0 - \epsilon'(\omega))^2 + (\epsilon''(\omega))^2]^{(1/2)},$$
$$u = [(\epsilon'(\omega) - \epsilon_\infty)^2 + (\epsilon''(\omega))^2]^{(1/2)},$$

$\epsilon'(\omega)$ is dielectric permittivity at particular frequency. A plot of $\log_{10}(v/u)$ versus $\log_{10}(f)$ as shown in figure 5(a) for the FLC-6980 gives a straight line, the intercept on the abscissa axis corresponds to the relaxation frequency. The relaxation frequency for GM and NRM are found to be 0.304 kHz and 325 kHz, respectively. The variation of the distribution parameter α as a function of temperature is shown in figure 5(b). It is interesting to note the effect of temperature on the relaxation frequency of GM, NRM and SM in figure 6(a,b). It can be observed that $(\delta\epsilon^{\mathrm{GM}})^{-1}$ and relaxation frequency for the GM and NRM is almost independent of the temperature but changes abruptly near transition for GM [figure 4(a,b)]. The decrease in the relaxation frequency with cell thickness indicates that the molecular motion would be restricted in the thin cell due to strong surface interactions. These results show that the dielectric parameters corresponding to GM are strongly dependent on temperature at T_{C^*A}. However, they are weakly dependent on temperature in SmC* phase.

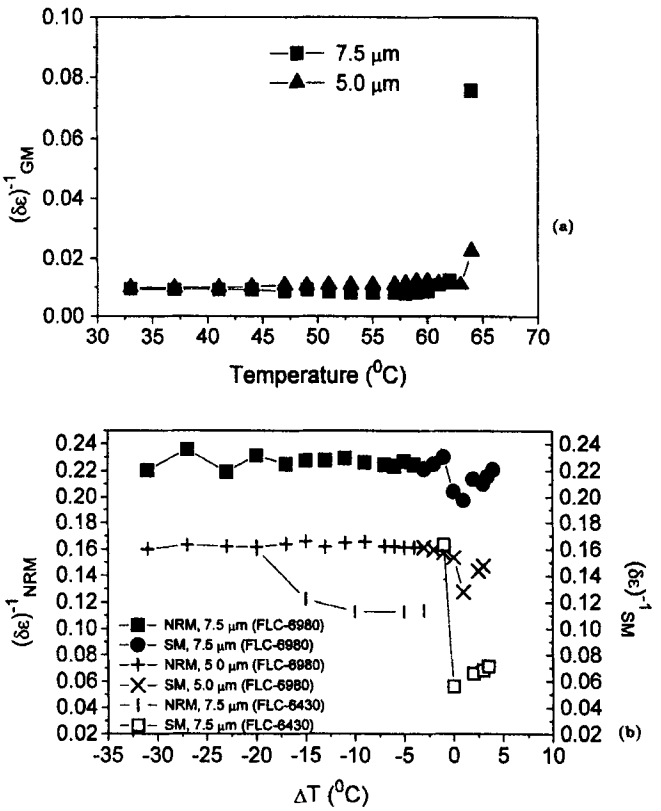


Figure 4. Temperature dependence of $\delta\epsilon^{-1}$ for (**a**) Goldstone mode, (**b**) soft mode and new relaxation mode for FLC-6980 and FLC-6430 sample at different cell thickness.

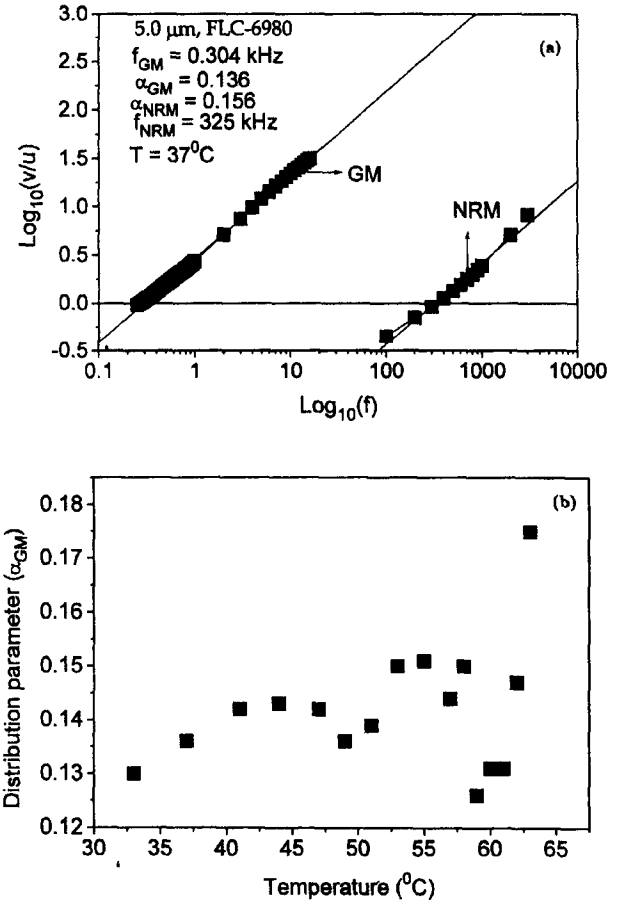
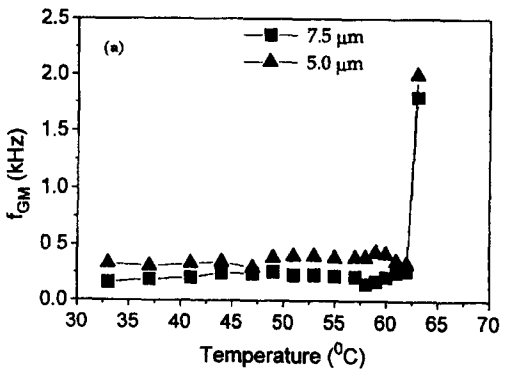


Figure 5. (**a**) Plot of $\log_{10}(v/u)$ versus $\log_{10}(f)$ for Goldstone mode and new relaxation mode at 37°C, (**b**) temperature dependence of the distribution parameter of Goldstone mode for 5μm cell thickness.



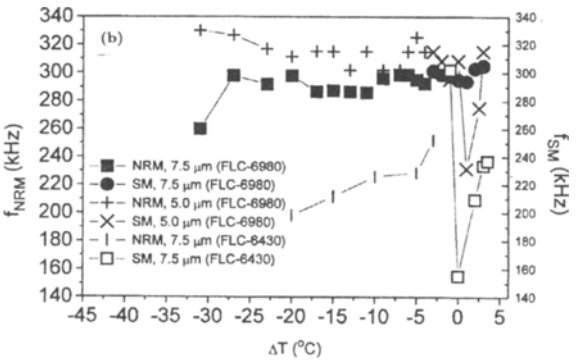


Figure 6. Temperature dependence of relaxation frequency for (**a**) Goldstone mode, (**b**) new relaxation mode and soft mode for FLC-6980 and FLC-6430 samples.

5. Conclusions

1. Dielectric relaxation modes have been studied in room temperature ferroelectric liquid crystal mixture possessing different material properties. The new relaxation mode has been investigated for the sample with different cell thickness.
2. The dielectric increment and relaxation frequency of NRM is almost independent of temperature but strongly depends on sample thickness. This mode is expected to have appeared due to the strong surface interaction and contribution from the tiny domains formed at the surfaces.
3. In SmC* phase, we have observed a new relaxation mode (NRM) whose dielectric increment at 37°C ($\delta\epsilon^{\mathrm{NRM}} \approx 6$) is small as compared to that for the GM ($\delta\epsilon^{\mathrm{GM}} \approx 103$). The relaxation frequency of this mode is about 325 KHz for 5μm thick cell at 37°C.
4. The dominant contribution to the dielectric constant is due to the GM and little contribution due to the NRM. Near the transition temperature Goldstone mode contribution to dielectric constant decreases rapidly. Above transition temperature, contribution to dielectric constant is only due to SM.
5. Near transition temperature, we found that the soft mode parameters satisfy the Curie–Weiss law.

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