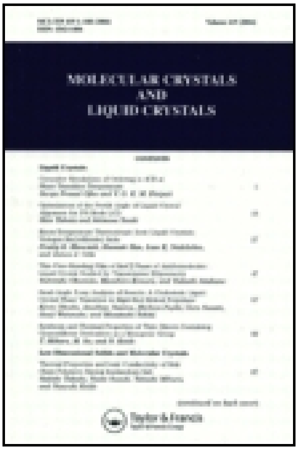

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Dielectric Relaxations in a Short Pitch Ferroelectric Liquid Crystal

K. K. Raina [a] & Jasjit K. Ahuja [a]

[a] School of Basic and Applied Sciences, Thapar Institute of Engineering and Technology, Patiala, 147 001, India

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Dielectric Relaxations in a Short Pitch Ferroelectric Liquid Crystal

K. K. RAINA* and JASJIT K. AHUJA

School of Basic and Applied Sciences, Thapar Institute of Engineering and Technology, Patiala-147 001, India

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Dielectric measurements in the frequency range 100 Hz to 100 kHz have been carried out in a short pitch ferroelectric liquid crystal mixture FLC-6430 (Hoffmann–La-Roche) in the SmC* phase aligned in planar orientation. The effects of temperature, frequency and bias voltage on the dielectric properties of this material have been investigated. The relaxation frequency *fr*, distribution parameter α and the dielectric strength ε_s have been determined. The calculated values were found to be ~0.59 kHz, 0.134 and 427.77 respectively for *fr*, α and ε_s at 45°C. A constant DC bias of 0.13 V/μm applied to the sample partially suppresses the Goldstone mode.

Keywords: Dielectric relaxation; ferroelectric liquid crystal mixture; short pitch; Goldstone mode; soft mode

1. INTRODUCTION

The ferroelectric properties in chiral smectic C (SmC*) liquid crystal (LC) phase were first demonstrated by Meyer *et al.*, in 1975 [1]. This state exhibits layered structure and appears by the formation of an incommensurate structure in the spatial distribution of molecular axis. The tilt of the molecular axis from the normal to the smectic layers precesses helicoidally while going from one layer to another. These systems are interesting from the view point of their physical properties [2–4] and use in display devices due to their fast switching speeds [5–7].

*Corresponding author. Tel.: +91-175-393116, Fax: +91-175-214498; e-mail: raina@tietp.ren.nic.in

Dielectric properties of ferroelectric liquid crystals (FLCs) hold a special interest in understanding the influence of the helicoidal texture on the static and dynamic properties of these systems. The earlier dielectric studies in FLCs were carried out in classic schiff base compounds [8]. Levstik *et al.* [9] explained experimentally and theoretically the presence of two relaxation modes "Goldstone mode" (GM) and "Soft mode" (SM) in these liquid crystalline materials. The "GM" appears in the SmC* phase due to the phase fluctuations in azimuthal orientation of the director while the "SM" appears near the transition temperature Tc* (SmC* – SmA* phase) due to the fluctuation of the amplitude of the tilt angle. It was also shown that the "GM" appears at low frequencies while the "SM" appears at higher frequency. Similar investigations have been reported by Carlsson *et al.* [10–11]. Biradar *et al.* [12] made a detailed study of the dielectric responses of a room temperature FLC mixture having low permanent polarisation. Dielectric studies on fluorinated compounds [13] having strong dipole moments attached to the chiral centres and highly ordered phases showed the presence of four relaxation modes in the SmC* phase. Wrobel *et al.* [14] reported the presence of a new relaxation process known as "new ferroelectric mode" (NFM) in a single component highly polar fluorinated compound where this mode is quiet strong. The NFM is connected with the formation of a special kind of modulated structure due to the tendency of the macroscopic spontaneous polarisation of smectic layers to compensate each other. In most of these materials, the "GM" dielectric increment was relatively large and it hindered the detailed study of the "SM" properties in the SmC* phase. This problem was overcome by applying a DC electric field [14–15] in the SmC* phase which suppressed the "GM". Gouda *et al.* [16] proposed a model for the determination of dielectric biaxiality in SmC* liquid crystals having uncompensated helix. This model is useful for developing correlation between molecular structure and their dielectric properties. Most of these studies are reported on the FLC's having low polarisation and long helical pitch but less attention has been paid to investigate the dielectric responses of room temperature FLC's having large spontaneous polarisation and short helical pitch. Efforts have been made by several research groups to understand the field effects, mechanism of switching and electro-optic characteristics in short pitch FLC materials [17–21] but their dielectric properties have not been studied in detail. Recently Markscheffel *et al.* [22] reported the measurements of the dielectric properties of a short pitch FLC compound in the direction of the helical axis. They showed that the dielectric biaxiality in this material was negative.

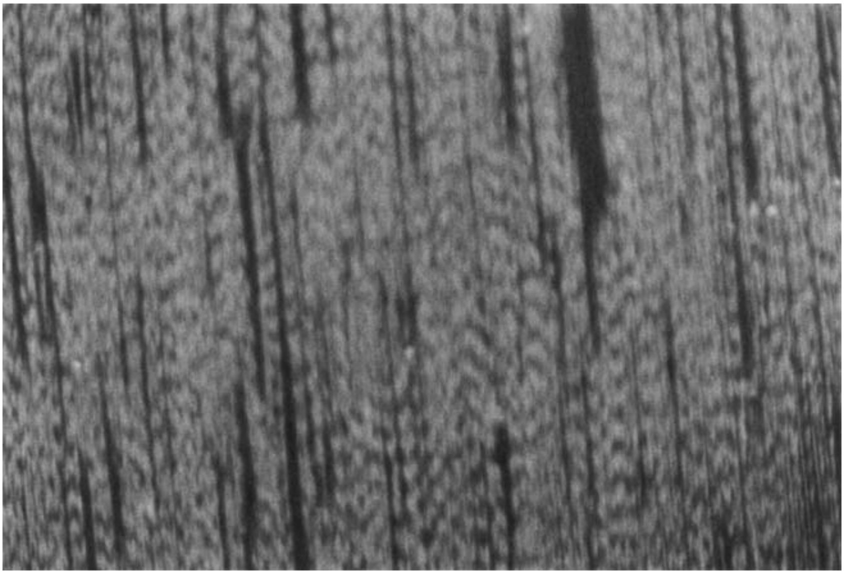
In this paper, the dielectric measurements in a large spontaneous polarisation and short pitch FLC materials are reported in the frequency range 100 Hz to 100 kHz. The sample was aligned in a planar orientation. The effects of temperature, frequency and bias voltage on the dielectric properties have been investigated. The relaxation frequency, distribution parameter and the dielectric strength have been calculated. Details of our experiment are given in Section 2 and the results have been discussed in Section 3. Conclusions have been drawn in Section 4 highlighting the need for further investigations.

2. EXPERIMENTAL

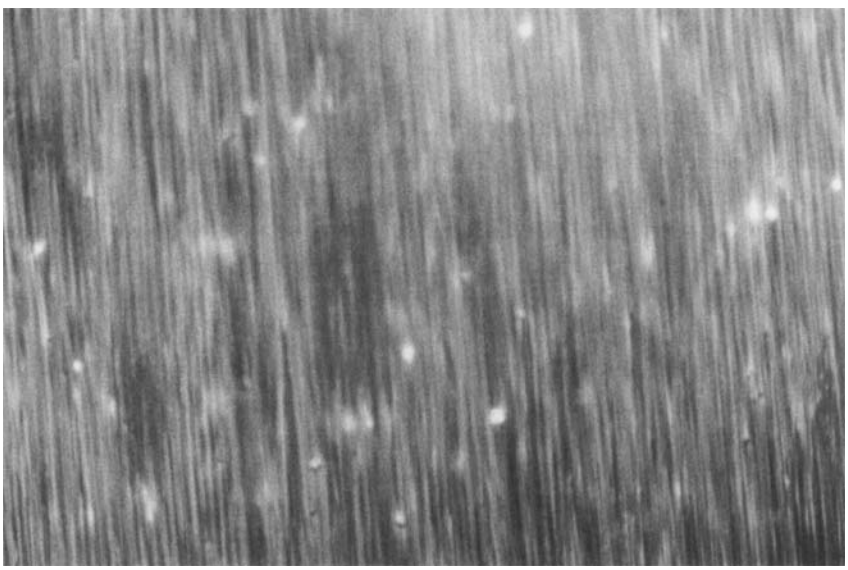
The frequency and temperature dependence of the real and imaginary part of the dielectric permittivity (ε' and ε'') have been studied in a room temperature ferroelectric liquid crystal mixture FLC-6430 (obtained from Hoffman - La Roche, Switzerland). At 22°C, its helical pitch is 0.43 μm, the spontaneous polarisation 90 nC/Cm^2 and the tilt angle 27°[17]. It has a wide SmC* temperature range given by the following phase diagram:

$$\text{Crystal} \xrightarrow{-11°\text{C}} \text{SmC}^* \xrightarrow{55°\text{C}} \text{SmA} \xrightarrow{64°\text{C}} \text{Isotropic}$$

These transition temperatures have been confirmed by studying its thermal polarising microscopy. The measurements have been carried out in a 7.5 μm thick sample sandwiched between two conducting Indium tin oxide coated glass substrates (LUCID, UK). These substrates have been pre-treated with the polyimide coating. The cells were filled by capillary action at the isotropic phase of the liquid crystal. The sample was then cooled into the SmA phase @ 0.1°C/min. in a LINKAM TP 90 and THS 600 temperature programmer cum hot stage. The thermal polarising microscopy of the sample was observed using GETNER polarising microscope. The optical texture of the sample in SmA and SmC* phase is shown in Figure 1(a, b). The complex electric permittivity was measured using Hewlett-Packard Impedance Analyser HP4192A in the frequency range 100 Hz to 100 kHz. The measurements have not been carried out at frequencies below 100 Hz to avoid DC conductivity effects. The cell was calibrated using air and benzene as standard references. Since we have carried our measurements only upto 100 kHz, it is observed that the "GM" contribution was dominant at lower frequencies. The studies of "SM" and other modes observable at higher frequencies are in progress.



(a)



(b)

FIGURE 1 Microphotograph of the optical texture of FLC-6430 (a) SmC*phase at 33°C and (b) SmA phase at 60°C in the absence of electric field. (See Color Plate X).

3. RESULTS AND DISCUSSIONS

3.1. Temperature Dependence of Dielectric Constant

The temperature dependence of dielectric constant ε' under a constant bias voltage 1.0 V at different frequencies is shown in Figure 2(a). It is seen that there is practically no dispersion beyond 55°C (*i.e.*, in the SmA phase) at all the frequencies studied. The dielectric constant attains saturation $\sim$ 10.52 at 10 kHz. The dispersion is more predominant at low frequencies ($\sim$ 1 kHz) and at low temperatures. This dispersion is attributed to the dominant "GM" contribution at these frequencies. At higher frequencies no variation in the dielectric constant has been observed throughout. Figure 2(b) shows the effect of bias voltage on the permittivity at 500 Hz and 1 kHz respectively. The effect of bias is well pronounced at both these frequencies. The decrease in permittivity is due to the suppression of the helical texture under the influence of the bias field.

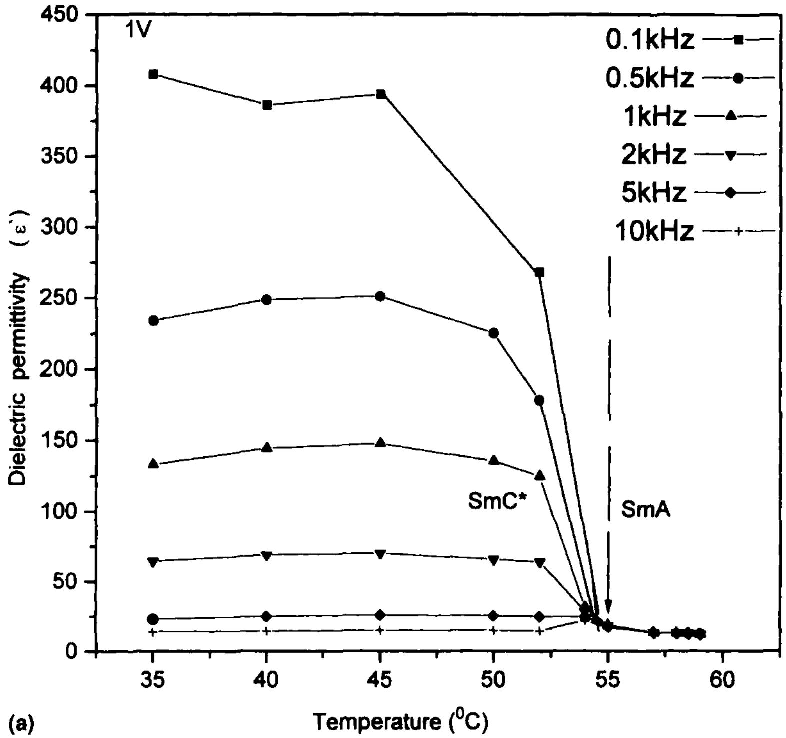


FIGURE 2 Dielectric permittivity (ε') real component as a function of temperature at different frequencies (a) at 1 V, (b) effect of bias voltage.

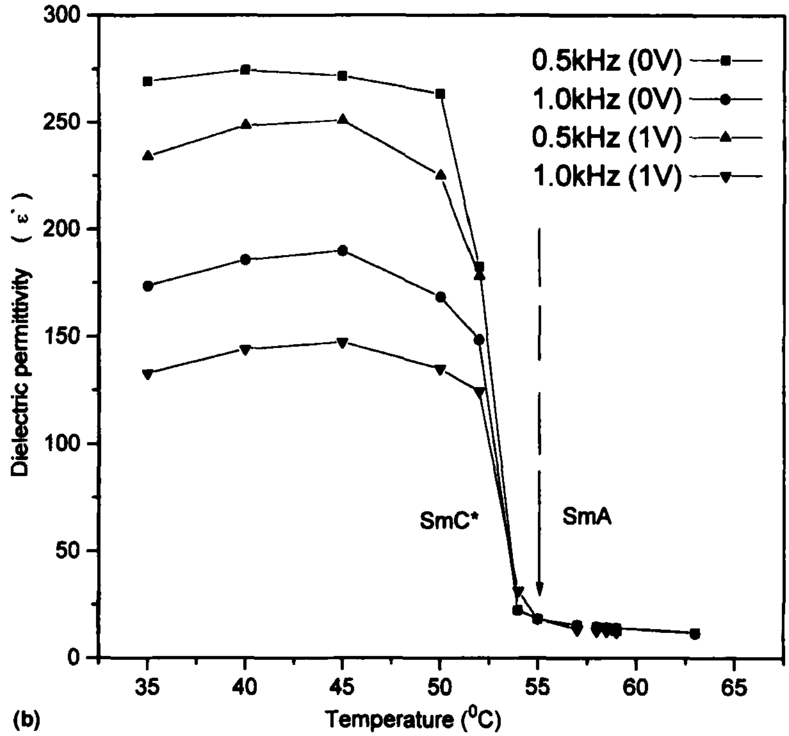


FIGURE 2 (Continued).

3.2. Effect of Frequency

The frequency dependence of the real part of permittivity (ε') at different temperatures is shown in Figure 3. It is seen that the permittivity decreases exponentially upto a frequency of ~3 kHz at all the temperatures in the SmC* phase *e.g.*, at 35°C we notice a change of about 390 in permittivity values while increasing the frequency from 100 Hz to 3 kHz. Thereafter it attains saturation. This dependence almost vanishes while approaching to Tc* *i.e.*, at 54°C (1°C below Tc*). Similar effect was seen at 55°C and 59°C (in the SmA phase) except that the values were smaller. All the measurements have been carried out at 1.0 V bias voltage.

Figure 4 shows the frequency dependence of the dielectric loss at different temperatures in FLC-6430. It is observed that the loss increases from 0.23 attains a maxima of ~2.33 at about 5 kHz at all the temperatures in the SmC* phase. *e.g.*, at 40°C, the maximum loss at 5 kHz was 2.33 while at 50°C it reaches to about 2.3.

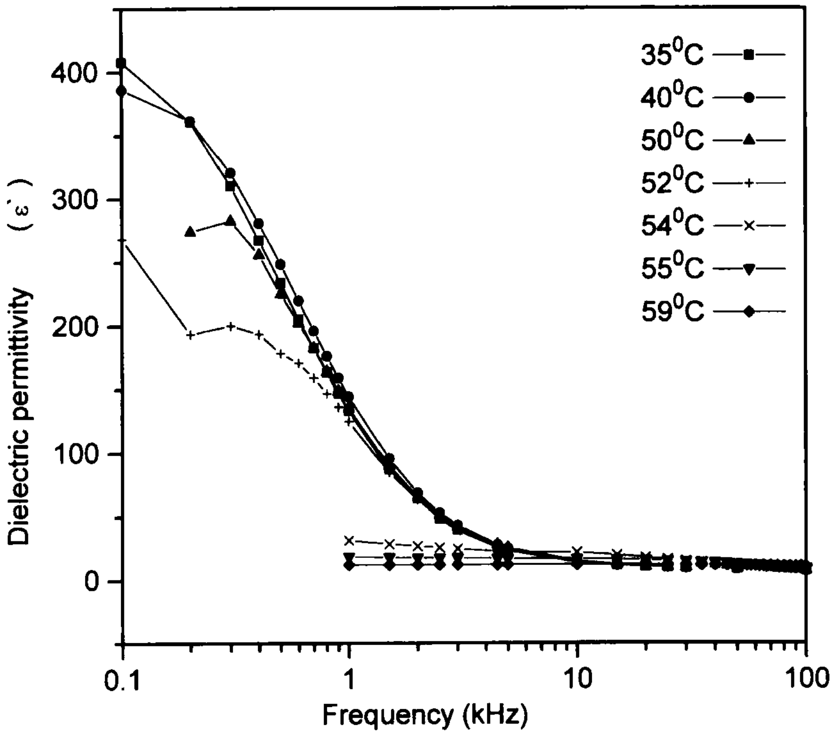


FIGURE 3 Dielectric permittivity ε` (real) as a function of frequency at different temperatures in SmC*and SmA phase.

As we approach the transition temperature (54°C), the loss peak at 5 kHz disappeared and shifts to higher frequency side. It is explained on the basis of the fact that both amplitude of the tilt and the azimuthal variations of the director becomes indistinguishable near Tc*.

Beyond 5 kHz, *e.g.*, at 50°C it is seen that the loss factor decreases from 2.3 to 0.82 and thereafter increases. It shows the possibility of the second loss peak in the higher frequency region. The second loss peak beyond 100 kHz is expected to be formed as a result of the new ferroelectric mode (NFM) also known as the domain mode or due to the surface mode. These modes have been observed by Wrobel *et al.* [14] in other ferroelectric liquid crystal mixtures. The investigations are in progress to give detailed explanation of these modes observed above 100 kHz.

The frequency dependence of the complex electric permittivity at different temperatures is shown in Figure 5. The imaginary part of dielectric constant (ε``) contributes to absorption and heat generation while the real part (ε`)

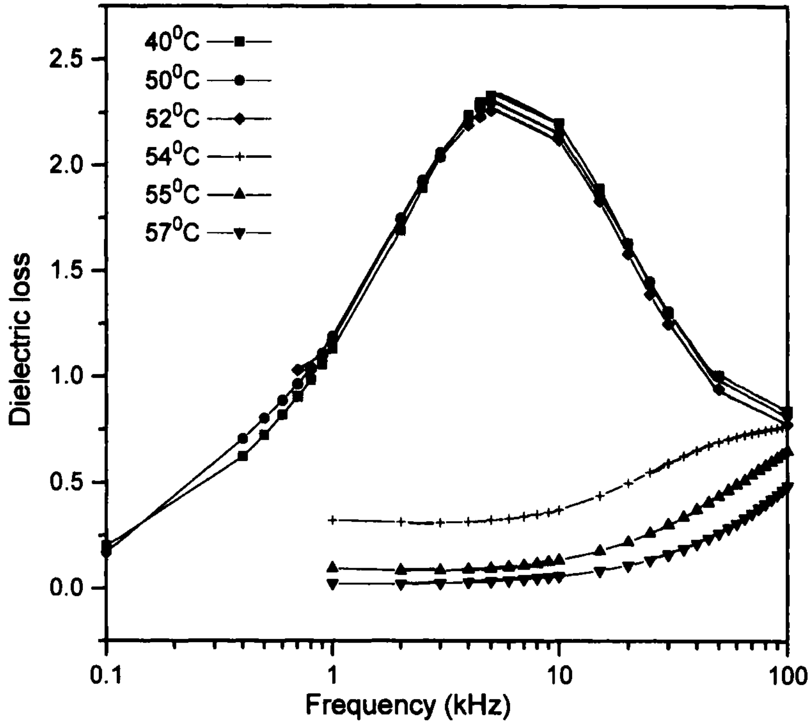


FIGURE 4 Dielectric loss as a function of frequency at different temperatures.

contributes to the dispersion. This heating effect may be large enough to change the physical properties of the liquid crystal materials. The absorption and dispersion in permittivity is reduced to a small value (~ 10) at frequencies beyond 10 kHz. The absorption peak is noticed to be ~ 0.6 kHz at 35°C that finally vanishes while increasing temperature towards Tc* in the whole spectrum. The trend in both dispersion and the absorption curves is very similar to that obtained for other FLC mixtures [13, 14, 22].

3.3. Effect of Bias Voltage

Figure 6 shows the effect of bias voltage on the dielectric properties of FLC-6430. It is seen that with the increase in the bias voltage from 1.0 volts to 10.0 volts, the contribution due to "GM" gets suppressed. The suppression is due to the partial unwinding of the helix at ~ 5.0 V which gets completely unwound at 10.0 V. Above this voltage the "surface mode" and "domain mode" may start appearing.

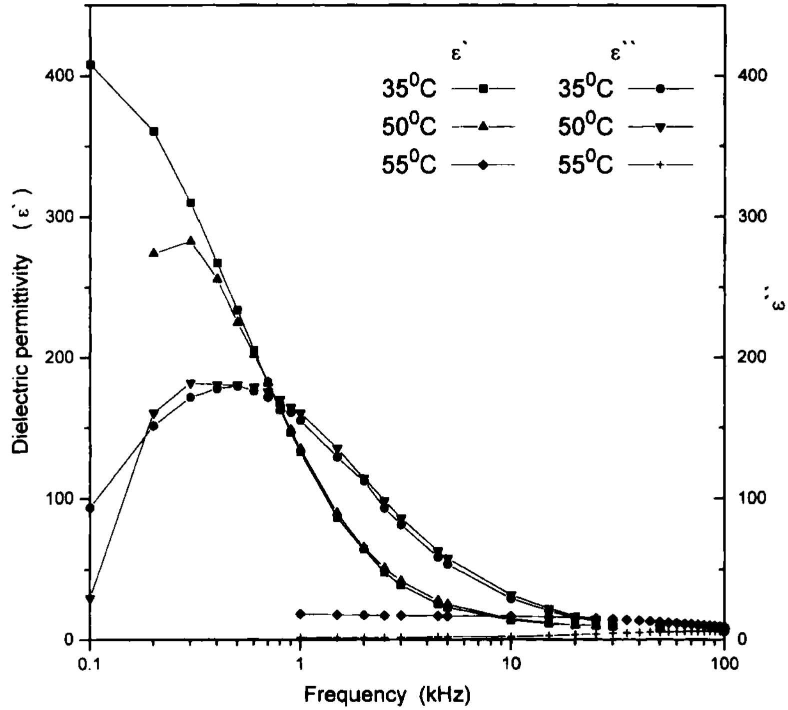


FIGURE 5 Absorption (ε'') and Dispersion (ε') plots as a function of frequency at different temperatures in SmC* phase of FLC-6430.

3.4. Dielectric Relaxation in SmC* Phase

A typical dielectric relaxation spectrum of the FLC-6430 mixture is reflected in the form of Cole–Cole plots indicating the single relaxation time of the molecules as shown in Figure 7. The 1.0 V bias partially suppresses the "GM" contribution. By fitting the experimental data points in the Cole–Cole equation the relaxation frequency and the distribution parameter has been calculated. It is interesting to note from the plot of the Figure 7 (inset) that at 54°C (near the transition) there is a simultaneous reflection of the two relaxation modes, one due to "SM" and other due to the "GM". The relaxation frequency (*fr*) and the distribution parameter (α) has been calculated using the Cole–Cole equation of the form [15, 20, 23].

$$\frac{V}{U} = (\omega\tau)^{1-\alpha} \tag{1}$$

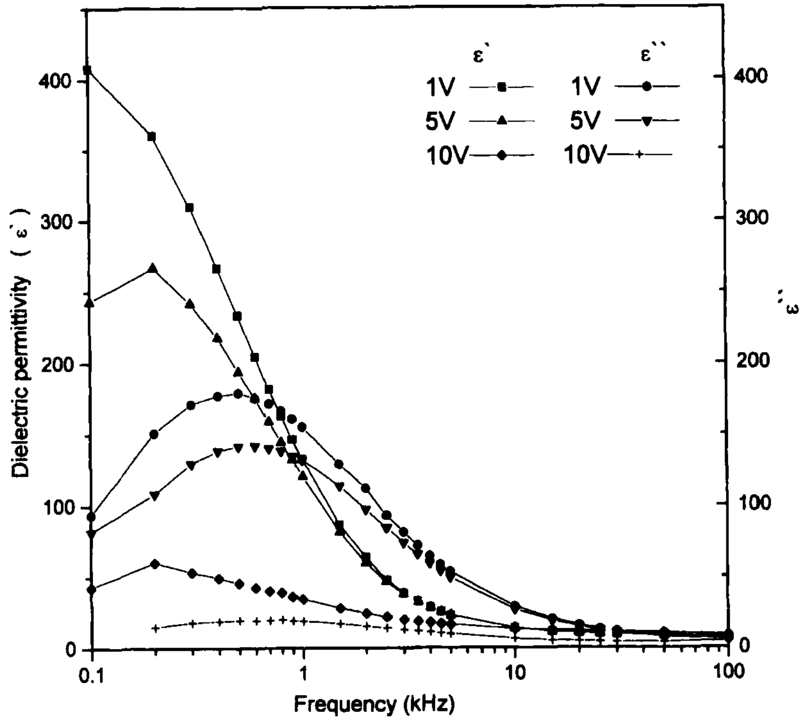


FIGURE 6 Frequency dependence of the permittivity component at varying bias voltages.

Where

$$V = [\{\varepsilon(o) - \varepsilon'(\omega)\}^2 + \{\varepsilon''(\omega)\}^2]^{1/2}$$
$$U = [\{\varepsilon'(\omega) - \varepsilon(\infty)\}^2 + \{\varepsilon''(\omega)\}^2]^{1/2}$$

$\varepsilon'(\omega)$ = Real dielectric constant at a particular frequency
$\varepsilon''(\omega)$ = Imaginary dielectric constant at that frequency
$\varepsilon(o)$ = Low frequency dielectric constant where the Cole–Cole plot cut the abcissa axis at the lower frequency side.
$\varepsilon(\infty)$ = High frequency dielectric constant where the Cole–Cole plot cut the abcissa at the higher frequency side.

A plot of $\log_{10}(V/U)$ *versus* $\log_{10}f$ gives a straight line as shown in Figure 8. The data points deviate from straight line because at low frequencies the

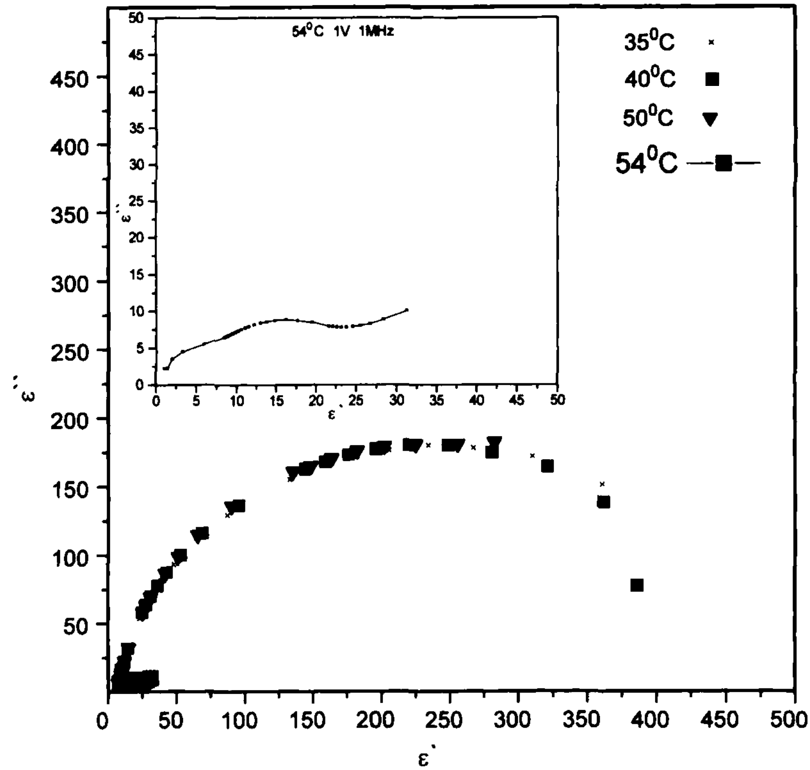


FIGURE 7 Cole–Cole plots of relaxation modes in SmC* phase at different temperatures (inset at 54°C) The Soft mode and Goldstone mode are clearly reflected.

value of (V/U) is very small as V is small however at higher frequencies (V/U) is very large and U is small. The intercept on the abcissa corresponds to f_r and the slope gives the distribution parameter α. In our sample α was found to be 0.14 at 30°C and 0.134 at 45°C.

A typical behaviour of the relaxation frequency as a function of temperature is shown in Figure 9(a). It is seen that the relaxation frequency remains almost constant upto about 52°C, thereafter it increases with temperature. This increase is rapid as we approach the transition temperature Tc*. The "GM" relaxation frequency is of the order of 0.6 kHz whereas the "SM" frequencies are in the range of 30 kHz and above at Tc*.

The temperature dependence of the dielectric strength of the short pitch sample under investigation in the SmC* phase is shown in the Figure 9(b).

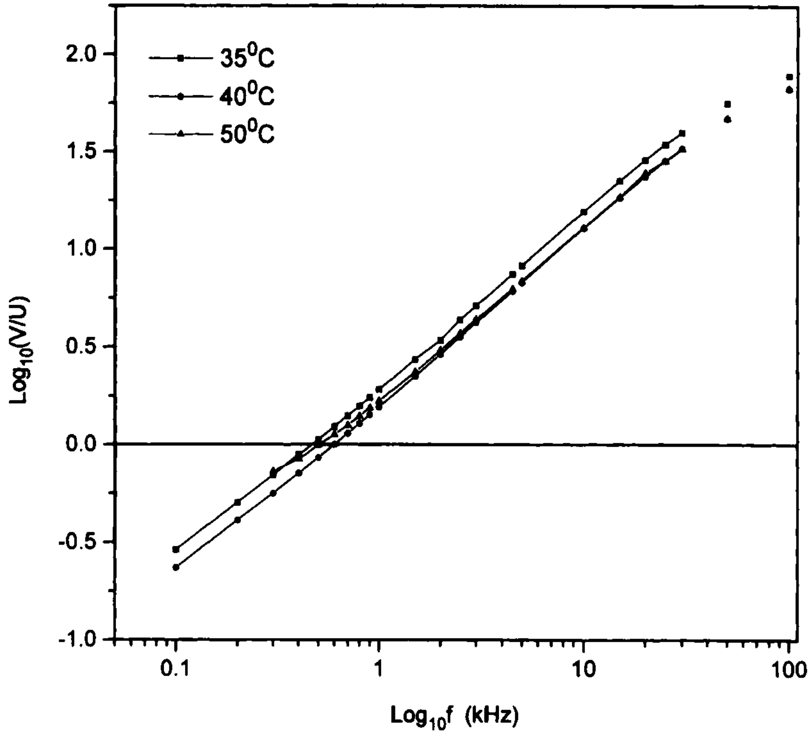


FIGURE 8 Plot of $\log_{10} f$ *Vs* $\log_{10}(V/U)$ for FLC-6430 at different temperatures.

Dielectric strength has been calculated using

$$\varepsilon_s = \varepsilon'(o) - \varepsilon'(\infty) \tag{2}$$

It is the maximum capacity of a capacitor to hold the charge and it is related to the susceptibility as

$$\chi = \varepsilon_o \varepsilon \tag{3}$$

where ε_o is the permittivity of free space.

It is observed that as we approach the transition temperature, the dielectric strength drops considerably to a very small value while the relaxation frequency of the molecules in the presence of the electric field near the transition temperature Tc* sharply increases to a very high value.

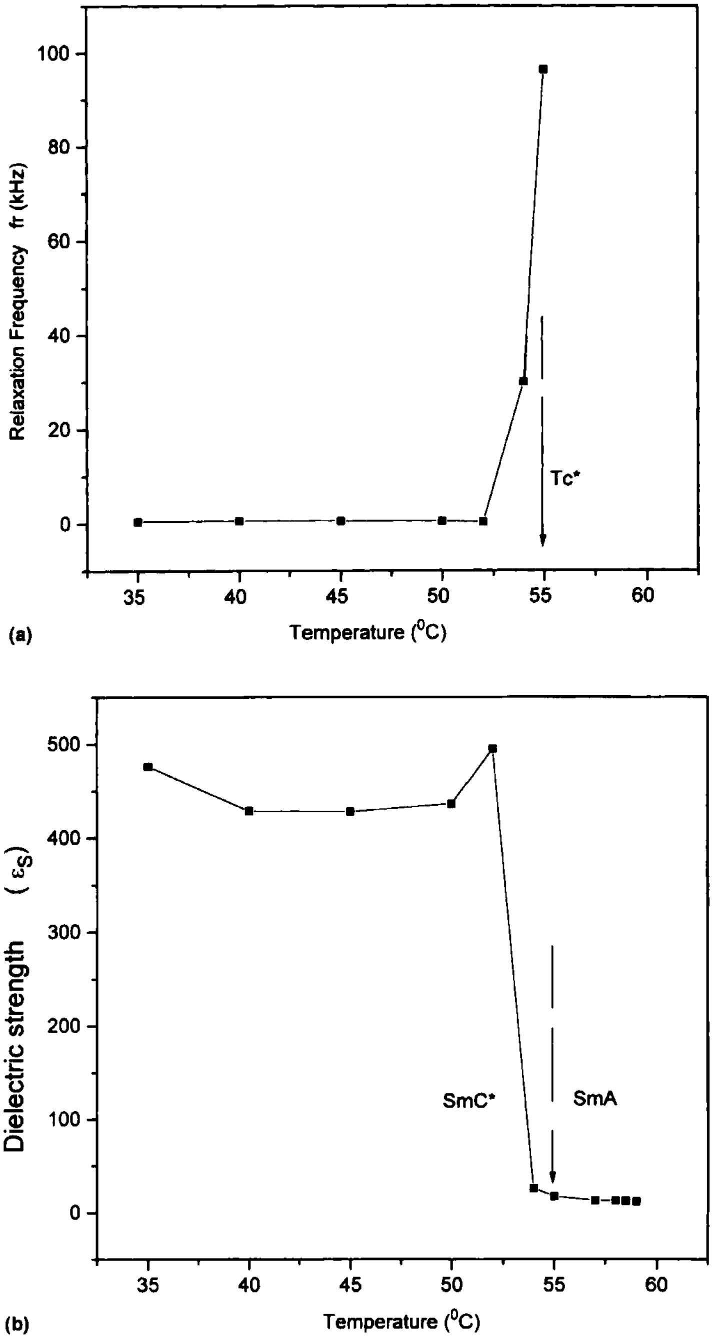


FIGURE 9 Temperature dependence of (a) relaxation frequency fr, (b) dielectric strength ε_s.

4. CONCLUSIONS

- ⋆ The dielectric permittivity measurements have been carried out in a novel short pitch FLC mixture in a 7.5 μm cell in planar alignment in the presence of a 1.0 V bias voltage. The bias field has been applied to partially suppress the "GM" as its dielectric increment is quite high.
- ⋆ The relaxation frequencies (*fr*), dielectric strength (ε_s) and distribution parameter (α) of the FLC material in the frequency range of 100 Hz to 100 kHz have been calculated. Their values are found to be 0.59 Hz, 0.134, 427.77 respectively at 45°C. These values were in good agreement with theory [20]. f_r varies slowly with increasing temperature in the SmC* phase due to the "GM" contribution while the dielectric strength decreases suddenly. The dominance of "GM" has been found at lower frequencies and at lower temperatures.
- ⋆ The results indicate that about 0.67 V/μm bias voltage is sufficient to suppress the "GM" of ferroelectric liquid crystal mixture FLC-6430. At higher bias voltages other modes like "surface mode" and "domain mode" may appear. It is being studied in detail upto 100 MHz.

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References

[1] R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. de. Phys* (*Paris*), **36**, L69 (1975).
[2] Ph. Martinot-Lagarde, R. Duke and G. Durand, *Mol. Cryst. Liq. Cryst.*, **25**, 2449 (1981).
[3] D. S. Parmar, K. K. Raina and J. Shankar, *Mol. Cryst. Liq. Cryst.*, **103**, 77 (1983).
[4] L. A. Bersenev, L. M. Blinov, M. A. Osipov and S. A. Pikin, *Mol. Cryst. Liq. Cryst.*, **158A**, 1 (1988).
[5] N. A. Clark and Sven T. Lagerwall, *Appl. Phys. Lett.*, **36**, 11 (1980).
[6] N. A. Clark, M. A. Handschy and S. T. Lagerwall, *Mol. Cryst. Liq. Cryst.*, **94**, 213 (1983).
[7] M. A. Handschy, N. A. Clark and S. T. Lagerwall, *Phys. Rev. Lett.*, **51**, 471 (1983).
[8] D. S. Parmar and Ph. Martinot-Lagarde, *Ann. of Physics*, **3**, 275 (1978).
[9] A. Levstik, T. Carlsson, C. Fillipic, I. Levstik and B. Zeks, *Phys. Rev. A*, **35**, 3527 (1987).

[10] T. Carlsson and B. Zeks, *Phys. Rev.*, **36**, 1484 (1987).
[11] T. Carlsson, B. Zeks, C. Fillipic and A. Levstik, *Phys. Rev. A.*, **42**, 877 (1990).
[12] A. M. Biradar, S. Wrobel and W. Haase, *Phys. Rev. A*, **39**, 2693 (1989).
[13] S. Wrobel, W. Haase, M. Pfeiffer, L. Beresnev and T. Geelhar, *Mol. Cryst. Liq. Cryst.*, **212**, 335 (1992).
[14] S. Wrobel, A. M. Biradar and W. Haase, *Ferroelectrics*, **100**, 271 (1989).
[15] Tapas Pal Majumder, Susanta Siha Roy, Subir K. Roy and Mukul Mitra, *Mol. Cryst. Liq. Cryst.*, **265**, 577 (1995).
[16] F. Gouda, W. Kuczynski, S. T. Lagerwall, M. Matuszczyk, T. Matuszczyk and K. Sharp, *Phys. Rev. Lett.*, **46**, 951 (1992).
[17] J. Funfschillig and M. Schadt, *Jpn. J. Appl. Phys.*, **30**, 741 (1991).
[18] K. K. Raina and H. J. Coles, *9th IEEE Int. Symp. on Appl. of Ferroelectrics*, USA, **PP788, CH3916-5**, 1995 IEEE.
[19] A. Jakli and A. Saupe, *Phys. Rev. E*, **35**, R5580 (1996).
[20] S. L. Srivastava, V. K. Agrawal, M. V. Loseva, N. I. Chernova and L. A. Beresnev, *Liquid Crystals*, **11**, 851 (1992).
[21] A. Jakli and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **263**, 103 (1995).
[22] Markscheffel, A. Jakli and A. Saupe, *Ferroelectrics*, **180**, 59 (1996).
[23] Vera V. Daniel, Dielectric Relaxation: Academic Press, New York, pp. 95–109 (1967).