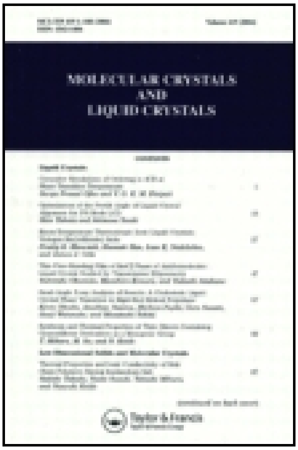

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Electro-Optic Effect and Influence of Bias Electric Field on the Goldstone Mode Dielectric Behavior in Smectic C* Phase and Cell Thickness Dependence of the Dielectric Permittivity of a Ferroelectric Liquid Crystal Mixture

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Results reported here on the spontaneous polarization, switching time, rotational viscosity and Goldstone mode dielectric strength and relaxation frequency as a function of electric field in the SmC^* phase of a Ferroelectric liquid crystal mixture. It has been observed that the spontaneous polarization and the rotational viscosity are almost independent of the amplitude of the applied field. The response time however depends on the applied field. The field required to unwound the helix is much larger than the structurally similar compounds. The dielectric strength of the Goldstone mode is found to decrease with the increase of bias electric field but the relaxation frequency of the Goldstone mode on the other hand increases with the increase of bias electric field. Results also show that the critical field E_C, for unwinding the helical structure in $SSMC^*$ phase depends on the temperature. Rotational Viscosity of the Goldstone mode has also been determined under D.C bias field in the SmC^* phase. Dielectric permittivity is found to increase with the increase of cell thickness. The increase of dielectric permittivity and the temperature of transition (T^*_C), in a thicker cell have also been explained considering theoretical relations developed earlier.

Keywords: Dielectric relaxation; electro-optic effect; ferroelectric liquid crystal

I. INTRODUCTION

The chiral Smectic C* (SmC*) phase of liquid crystal molecules gained an increasing amount of interest during last two decades and much effort has been made to characterize the basic thermodynamic properties of these system. Ferroelectric Liquid Crystal [FLC] molecules have been extensively studied by means of dielectric spectroscopy,[1-5] but not too many papers are seen to have published on the studies of the dielectric behavior of FLC molecules under bias electric field and by varying the thickness of the dielectric cell. Bias dependent dielectric studies provide important information regarding the existence of additional modes in the SmC* phase of FLC materials. The dominant Goldstone mode appears due to the fluctuation of the azimuthal angle (φ) of the director around the helical axis in a planar aligned Cell. The weaker modes of vibrations in SmC* phase can not be observed due to huge fluctuation of azimuthal angle. Bias field helps to unwind the helical structure and as a result there will be a little or no φ-fluctuation. Any weaker mode if presents in SmC* phase, can only be observed after applying bias electric field. It is also experimentally observed that both tilt and the spontaneous polarization are affected by the application of bias electric field and so as the dielectric permittivity of the material. The thickness of the measuring cell plays a significant role on the dielectric properties of FLC because it affects the helical strucure, the transition temperature[6,7] and the magnitude of spontaneous polarization[8,9]. An extensive physical chaterization was carried out on a FLC mixture ZL4655-000, including the measurements of spontaneous polarization, rotational viscosity and switching time as a function of temperature and measuring electric field. Goldstone mode dielectric behavior as a functionof temperature, bias electric condition, cell thickness are also reported in this paper. Rotational viscosity has also been determined from polarization reversal method and dielectric method and the results are included in this paper. The studied ferroelectric liquid crystal mixture ZLI 4655-000 is obtained from E Merck. The sample possesses low spontaneous polarization (= 7 nC cm^{-2} at 20^0 C). The phase sequences of the sample are as follows (Ch denotes cholesteric, I isotropic, and K crystal)

K<-10^{0}C Sm-C* 60^{0}C Sm-A* 69^{0}C Ch 72^{0}C I

II. EXPERIMENTAL

The polarization measurement was carried out with a planar aligned cell (EHC. Co.) having a thickness 10 μm and an active area 16 mm^2. Dielectric measurements were carried out in different cells. The ferroelectric liquid crystal samples were held between two conducting glass plates whose surfaces had been treated properly for obtaining planar alignment. We have used indium-tin oxide coated cells having a separation of 6 μm and 100 μm and gold coated glass cell having a separation of 17 μm. A good planar alignment was achieved by slowly cool it down from isotropic temperature to room temperature and simultaneously applying a low frequency field. The temperature of the sample was stabilized to an accuracy of the order of 0.1^0 C. A Hewlett-Packard impedance analyzer HP 4192A working in the frequency range of 5 Hz to 13 MHz was used for the complex dielectric permittivity measurements. Before putting the sample into the cells, the air capacitance for the two cells were recorded at mixture possesses a low P_S value, so we could not excite the Goldstone mode with low ac measuring voltage. A measuring voltage of 1 Volt was applied in a direction parallel to the smectic layers for measuring dielectric permittivities at different bias field. The stray capacitance for each cell was measured by using spec-pure benzene.

III. RESULTS AND DISCUSSION

A) Electro-optic effect

Spontaneous Polarization (P_S) and Switching time have been determined by the polarization reversal method. A square wave voltage of frequency 60 Hz and a varying amplitude of minimum 30 volts was necessary to achieve sufficient ferroelectric torque that could unwound the helix because of the low spontaneous polarization of the material. A good polarization reversal current bump was only obtained at about 30 V_{rms}. The signal has been taken across 10 KΩ resistor and is fed to HP digitizing oscilloscope from where the wave form was transferred to a computer. The area has been measured in microcal origin creating appropriate base line. The value of polarization obtained in this way was in good agreement with the literature value at a particular temperature. Viscosity was determined from the measured value of polarization and switching time using the relation[10]

$$\tau_\phi = \frac{\gamma_\phi}{P_S E}, \qquad (1)$$

where τ is the reorientational time, η is the viscosity, P is the polarization and E is the eletric field.

Spontaneous polarization (P_S), viscosity (η_ϕ) and switching time (τ_ϕ) are found consistent with the literature value and as usually decrease with increase of temperature as shown in Figs. 1a, 2a & 3a.

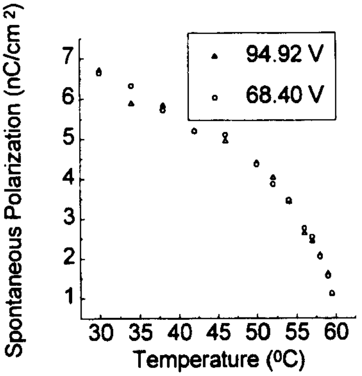

FIGURE 1a. Variation of Spontaneous polarization with temperature at two different applied voltage

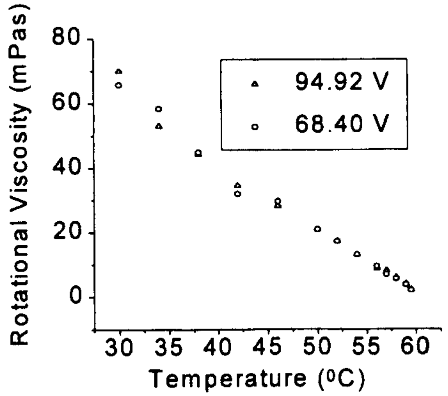

FIGURE 2a. Variation of rotational viscosity with temperature at two different applied voltage

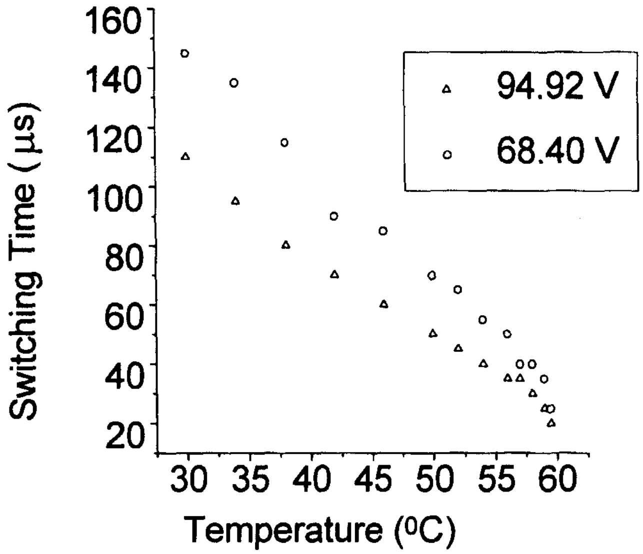

FIGURE 3a. Variation of switching time with temperature at two different applied voltage

Viscosity and P_S were determined at two different measuring field. It has been observed that both the spontaneous polarization and viscosity of the compound do not change with the change of the amplitude of the square wave field as shown in Fig.(1a & 1b) and Fig (2a & 2b),but the switching time decreases with field (Fig.3b). The decrease of switching time with increase of applied voltage can be explained if the response time in ferroelectric interaction with electric field. is considered as defined by the above Eq. (1). Since P_s and γ_ϕ were found independent of electric field, so an increase of the applied voltage decreases the switching time. When a square wave voltage of appropriate amplitude and frequency around 60Hz is applied to the cell, first it unwounds the helix and the dipoles are then lined up and started switching due to square wave pulse. Polarization reversal current is dominating and induce a current bump. The area of polarization reversal current bump gives the measure of the spontaneous polarization. The dipoles are already lined up with the applied square wave field of amplitude 30 V_{rms}, so a further increase of the amplitude of the field does not create any change of polarization of the compound which has been observed in the present study and shown in Figs. 1a & 1b. Viscosity showed almost the similar dependence with applied field

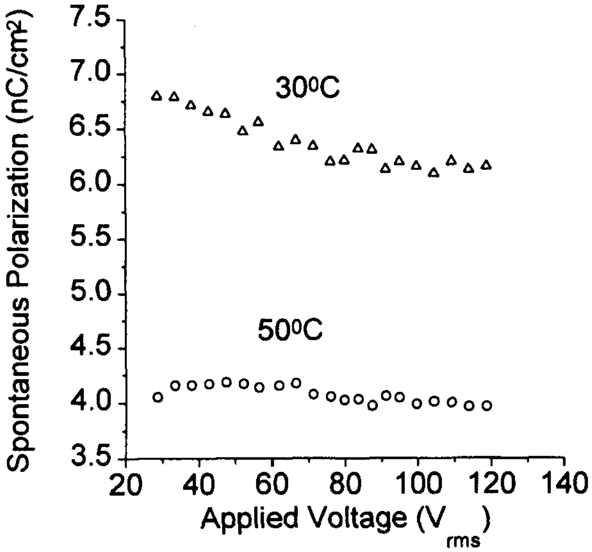

FIGURE 1b. Variation of spontaneous polarization with applied voltage at two different temperatures

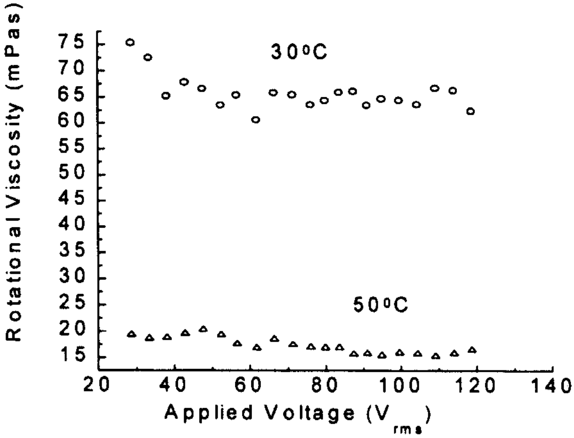

FIGURE 2b. Variation of rotational viscosity with applied voltage at two different temperatures

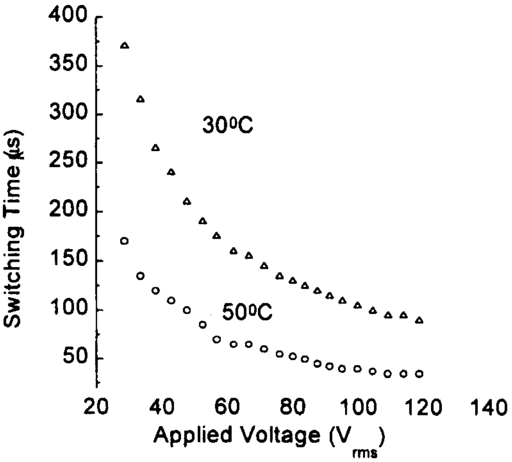

FIGURE 3b. Variation of switching time with applied voltage at two different temperatures

(Figs. 2a & 2b). Switching field is rather high in this compound due to low spontaneous polarization of the FLC mixture.

B) Effect of bias electric field on the Goldstone mode dielectric strength ($\Delta\epsilon_G$), relaxation frequency (f_G) and rotational viscosity (γ_φ) in the Smectic C* phase.

In a planer aligned cell when the measuring field is parallel to the layer plane in SmC* phase, the main contribution to the polarization comes from the Goldstone mode process that arises due to huge phase angle (φ) fluctuation. By plotting ε' (the real part of the dielectric permittivity) vs. ε'' (imaginary part of the dielectric permittivity) in a Cole-Cole[11] diagram at different temperatures, the relaxation frequency as well as the dielectric strength of Goldstone mode in SmC* phase have been determined at different bias electric field. The measurements were carried out at two temperatures, one at 50^{0}C (10^0 C below the T_C^*), where the softmode contribution is negligibly small and other at 59^{0}C (1^0 C below the T_C^*) where there may have some soft mode contribution. Bias field dependence

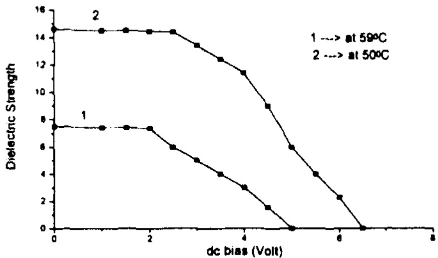

FIGURE 4. Variation of Goldstone mode dielectric strength ($\Delta\varepsilon$) with dc bias at cell thickness 6μm.

of Goldstone mode dielectric strength ($\Delta\epsilon_G$) and relaxation frequency (f_G) are shown in Fig. 4 and Fig. 5 respectively. It is observed from the Fig. 4

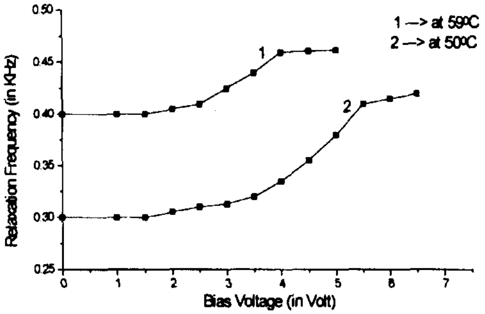

FIGURE 5. Variation of Goldstone mode relaxation frequency with dc bias at cell thickness 6μm.

that $\Delta\epsilon_G$ does not change significantly from 0 Volt to 2 Volt. However a further increase of dc bias from 2 volt to 4 volt decreases $\Delta\epsilon_G$ linearly. At still higher dc voltage, $\Delta\epsilon_G$ abruptly falls to a minimum. Finally above 4.5V and 6V $\Delta\epsilon_G$, becomes almost zero at temperature 59°C and 50°C respectively. The above results can be explained as follows. At lower bias voltages (below 2V) helix remains unaltered resulting no significant change in dielectric strength. In the region of 2V-4V bias fields $\Delta\epsilon_G$ decreases linearly, showing a slow and continuous deformation of the helix. Finally very near to the critical unwinding field E_C, the effect becomes strongly nonlinear and $\Delta\epsilon_G$ falls to a minimum value. Above $E \geq E_C$ all the dipoles are lined up along the field and there is a complete unwound of the helical structure. Therefore the measured dielectric strength of the Goldstone mode is essentially zero. Without the bias field, relaxation frequency in SmC* is almost constant with temperature. Fig. 5

also shows an invariance of relaxation frequency at lower bias field, when the bias field does not affect the helical structure. The relaxation frequency however increases with further increase of bias field which is the manifestation of the distortion in azimuthal angle φ. It is also observed from our results and the results published elsewhere for other materials[12, 13] that critical field for complete unwinding of the helix depends mainly on the P_S of the materials which is also indicated from relation between the bias electric field E_C and the material parameters is given by

$$E_C = \pi^2 K \theta^2 q^2 / 16 P_S \qquad (2)$$

where $K\theta^2 q$ = elastic energy associated with pitch in the SmC* phase and that does not vary too much for material to material. E_C thus depends mainly on the spontaneous polarization of the material. The critical unwinding field at 10°C and 1°C below T_C^* is around 7V and 4V respectively. Far away from T_C^* in SmC* phase the helix is tightly bound and the structure is stable, the bias thus required to unwound the helical structure is higher. On approaching to T_C^* molecular fluctuation increases and less energy is therefore required to unwound the helix. Rotational viscosity has been calculated using the Visco elastic equation[3]

$$\gamma_\phi = P^2 / (4\pi\theta^2 \Delta\epsilon_G f_G) \qquad (3)$$

where P= Spontaneous polarization, θ= tilt angle, $\Delta\epsilon_G$ and f_G have their usual meaning and γ_ϕ is the viscosity coefficient of the material. We have taken the literature[14] values of P_S and tilt angle (θ) and neglected a small variation of these parameters with bias field. The variation of rotational viscosity with DC bias voltage is shown in Fig..6.

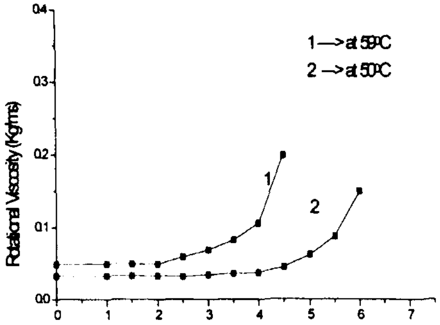

FIGURE 6. Variation of rotational viscosity with dc bias at cell thickness 6μm

It is shown in Fig. 6 that γ_ϕ does not change upto a certain bias voltage (2 volts). From 2 volt to 6 volt it gradually increases towards maximum value. Helicoidal structure remains unchanged upto a certain bias voltage and the value of parameters involved in Eq. (3) does not change and γ_ϕ remains unaltered but above 2 volts due to a continuous deformation of the helical structure, $\Delta\epsilon_G$ diminishes to a lower value. Since $\Delta\epsilon_G$ involved in the denominator of Eq. (3), γ_ϕ therefore increases linearly. The other parameters involved in Eq. (3) do not affect the value of γ_ϕ as much as that of $\Delta\epsilon_G$.

C) Cell thickness dependence of the dielectric permittivity

The temperature dependence of dielectric permittivity in SmC* phase at 100Hz for the cells of thickness 6, 17 and 100μm are shown in Fig. 7. It is observed from the Fig. 7 that the magnitude of dielectric constant ε' and the temperature of transition increase with the increase of cell thickness. A small peak of dielectric permittivity has been observed at the temperature of transition between SmA*- SmC*, phase (Fig. 7) and the peak becomes prominent in smaller thickness of the cell. In a thinner cell, the helicoidal structure in the SmC* phase becomes unwound due to the wall effect and the contribution of the Goldstone mode is suppressed, resulting a prominence of the peak of dielectric permittivity. Such characteristic peak was also reported earlier[12,15] by a few authors.

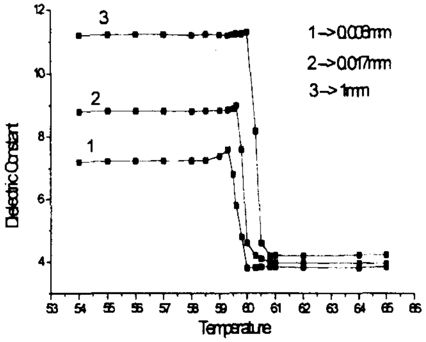

FIGURE 7. Temperature dependence of dielectric constant without bias at different sample thickness.

Recently, we have developed a theoretical relation[16] from the Landau free energy expansion between SmC*-SmA* phase transition temperature (T_C^*) of chiral smectic compound and that of its nonchiral analogue which is as follows.

$$T_C^* = T_C + \frac{C^2\chi_0}{\alpha'} + \frac{P^2\Omega}{\alpha'}, \tag{4}$$

where T_C^* is the SmC*- SmA* phase transition temperature. T_C is the SmC-SmA phase transition temperature. $\alpha^{/}$ is the mean-field coefficient, χ_0 is the high frequency dielectric susceptibility, C is the piezoelectric bilinear coupling term and Ω is the biquadratic coupling term between tilt and polarization. It was shown that the bilinear and the biquadratic couplings between tilt and polarization are responsible for the increase of the T_C^* of a chiral compound in comparison to that of its non-chiral analogue.

Again, the cell thickness dependence of the spontaneous polarization of FLC compound was also derived in one of our earlier paper[17], which was written as,

$$P = \left(P_{\max}\right)^2 - \left(\frac{\pi^2 g}{2\Omega}\right)\frac{1}{\left(d + \frac{2g}{|W|}\right)^2}\Bigg)^{\frac{1}{2}} \qquad (5)$$

where g is the elastic modulus, W is the effective anchoring energy and $(P)_{\max}$ is the maximum polarization. When $|W|d >> g$, we have

$$P = \left(\left(P_{\max}\right)^2 - \left(\frac{\pi^2 g}{2\Omega}\right)\frac{1}{(d)^2}\right)^{\frac{1}{2}}. \qquad (6)$$

At $|W|d << g$ the dependence of spontaneous polarization (P) on cell thickness is very small.

The shift of the transition temperature T_C^* at the different thickness of the measuring cell can be explained by considering Eq. (4) and (6), where the polarization in the right hand side of the Eq. (4) depends on the thickness of the cell, so an increase of cell thickness, increases the spontaneous polarization and that in turn increases T_C^* in a thicker cell. The increase of dielectric permittivity with the increase of cell thickness (Fig. 7) can also be explained considering the above Eq. (6). The relation states that in a surface stabilized structure of the cell the polarization is increased when the thickness of the cell increases, resulting an increase of permittivity. Again in a still thicker cell the helical structure is not suppressed and there is a maximum contribution from Goldstone mode process result in an increase of the permittivity.

IV. CONCLUSION

The Electro-optic and dielectric dielectric behaviour of the FLC mixture (ZLI-4655-000) in SmC* phase as a function of temperature and bias electric field and were investigated. It has been observed that the spontaneous polarization and rotational viscosity do not change with the increase of applied square wave field but the switching time decreases with the applied field. It has also been observed that at lower bias field the Goldstone mode dielectric strength and relaxation frequency do not change as long as the bias field does not affect the helical structure. A further increase of bias field, there is a gradual deformation of the helical structure and as a result the dielectric strength decreases, but relaxation frequency increases to a maximum value. A small peak of the dielectric permittivity has been observed at T_C^* and it becomes prominent in a thin cell. It is interpreted as due to the softmode contribution and which becomes prominent after suppression of the Goldstone mode in a thin cell due to surface effect. The temperature of transition (T_C^*) between SmC*-SmA* phase increases with the increase of cell thickness.

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