Collective dielectric processes at the transition temperature of the Sm-C^* and Sm-A^* phase in a ferroelectric liquid crystal

Lokesh K. Gangwar,[1,2] Ambika Bawa,[1,2] Amit Choudhary,[3,*] Surinder P. Singh,[2] Rajesh,[2] and Ashok M. Biradar[2,†]

[1]*Academy of Scientific and Innovative Research (AcSIR), CSIR–National Physical Laboratory (CSIR-NPL) campus, New Delhi-110012, India*

[2]*CSIR–National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi-110012, India*

[3]*Physics Department, Deshbandhu College (University of Delhi), Kalkaji, New Delhi-110019, India*

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An anomalous dielectric relaxation process, called the partially unwound helical mode (p-UHM), is a collective dielectric process apart from the well known Goldstone and soft mode process; it is studied in the smectic C^* (Sm-C^*) phase and at the transition temperature of the Sm-C^*−Sm-A^* phase in the ferroelectric liquid crystal (FLC) material. To avoid the surface effect, a thick cell of 40 μm thickness was prepared with highly rubbed surfaces of the ITO substrates. It has been observed that the dielectric properties in Sm-C^* and at the T_c temperature are dominated by the p-UHM process which is dependent on an applied oscillating field in the Sm-C^* phase. The probing ac and dc bias field dependences of all these collective dielectric processes have been reported in the Sm-C^* and Sm-A^* phases of FLC materials.

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I. INTRODUCTION

Ferroelectric liquid crystals (FLCs) are promising materials from basic and applied aspects. Although the FLC materials were discovered as long as four decades ago by Meyer *et al.* [1], their applied aspects were not fully exploited due to the complexity in their molecular structures. Nematic liquid crystals are being used commercially, whereas the FLCs were not commercialized as compared to nematic LCs which could be due to the complexity in the layering and helicoidal arrangement of the molecules. The FLC materials have been mainly characterized by the electro-optical and dielectric spectroscopy techniques. The triangular wave method is used to study *spontaneous polarization* whereas the electro-optical technique is used to study the *optical properties* like optical contrast, switching time, memory effect, etc. [2,3]. On the other hand, dielectric spectroscopy is used for studying the *molecular dynamics* of the liquid crystal materials.

Dielectric spectroscopy is a versatile technique for characterizing molecular dynamics of FLC materials as the collective dielectric processes are observed in the frequency range of a few hertz to a few kilohertz, whereas the ionic conductivity and contact resistance interference is observed at subhertz to a few hertz. The collective dielectric processes in FLC materials are due to helicoidal structure and tilt angle of the materials. The main collective dielectric processes reported in the literature are due to the phase fluctuation or Goldstone mode and tilt angle fluctuations, called the soft mode [4,5]. The other dielectric processes in FLC materials are the molecular relaxation around the short and long molecular axes, which is observed in homotropic and planar alignment of molecules, respectively, and lies in the range from mega- to gigahertz frequency like in nematic liquid crystals [6]. The helix related dielectric phenomena are scarcely reported in the literature [7], although it is an important parameter for showing ferroelectric behavior in liquid crystal materials.

The helical unwinding process has shown more closeness to the fixed pitch theoretical model rather than the diverging model [8]. The winding process is found to be slower than the unwinding process as revealed by the studies of asymmetric square pulse [9]. The experimental observations have shown abrupt changes in biaxiality and tilt angle before a complete helical unwinding of helix as revealed by conoscopy of 4-(1-methylheptyloxycarbonyl)phenyl4-octyloxybiphenyl-4-carboxylate (MHPOBC) FLC [10].

In the present investigations, the collective dielectric relaxation processes of FLC have been studied in the smectic C^* (Sm-C^*) phase and at the phase transition temperature (T_c) of the Sm-C^*−Sm-A^* (smectic A^*) phase. The main collective dielectric processes due to phase and tilt fluctuations have been studied at low and high probing ac fields. In addition to these two collective processes, one more dielectric mode is added due to helicoidal mode fluctuations called the partially unwinding helical mode (p-UHM) in Sm-C^* and at the transition temperature of the Sm-C^*−Sm-A^* phase. This process appears to be due to the varied helicoidal structure near the bounding substrate and in the bulk of the sample cell. As suggested in the earlier report [11], the surface effect plays a dominant role for the detection of the p-UHM process. However, in the present manuscript, not only the surface effect but the helix of the material is also responsible which is shown even in a thick cell (40 μm) and can be seen clearly near the T_c temperature in the Sm-C^* phase as the helix of the material becomes soft. The contribution of the dielectric permittivity of the p-UHM process with low and high oscillating field is studied in details. The effect of a bias field on all the three collective dielectric processes is emphasized in Sm-C^* and at the T_c temperature as the soft mode (tilt fluctuations) appears

*amitnpl2005@gmail.com
†abiradar.npl@gmail.com

only near the transition temperature of the Sm-C^*−Sm-A^* phase.

II. EXPERIMENT

Highly conducting and transparent indium tin oxide (ITO) coated glass plates were used for making the electrodes. A desired pattern of a square shape (2 mm × 2 mm) was prepared on conducting ITO glass plates using a photolithographic technique. Nylon 6/6 was coated on the glass substrates and strongly rubbed along the desired direction for planar alignment. The thickness of the cell was maintained around 40 μm by using a Mylar spacer. The FLC material, KCFLC-10S, was filled into the cell by capillary action by heating it at the isotropic phase temperature and then the cell was cooled down gradually to room temperature. The KCFLC-10S material has the following phase sequence as per the data sheet:

$$\text{Crystalline} \overset{7\,^\circ\text{C}}{\longleftrightarrow} \text{Sm-}C^* \overset{64.5\,^\circ\text{C}}{\longleftrightarrow} \text{Sm-}A^* \overset{99.5\,^\circ\text{C}}{\longleftrightarrow} \text{Nematic} \overset{112\,^\circ\text{C}}{\longleftrightarrow} \text{Isotropic}.$$

The material has a pitch value of ∼2.5 μm and spontaneous polarization (P_s) of 23nC/cm^2 at room temperature (25 °C). The alignment of the liquid crystal molecules was checked under crossed polarizers in a polarizing microscope (Carl Zeiss, Axioskop 40A, Germany) and confirmed a homogeneous (planar) alignment. The dielectric measurements were taken using an impedance analyzer (Wayne Kerr 6540A, UK) in a frequency range of 20 Hz to 1 MHz with a measuring peak-to-peak voltage from 30 mV to 1 V. A uniform temperature of the sample was maintained by a temperature controller (JULABO F-25 HE, Germany) with an accuracy of ±0.1 °C for the experiments.

III. RESULTS AND DISCUSSIONS

It is well known that the collective dielectric processes in the Sm-C^* phase are due to helicoidal structure and tilt angle of the material and are called the Goldstone mode and soft mode, respectively. The other collective dielectric process is the domain mode, reported by Haase's group [12] also due to helicoidal structures, which breaks into different domains in high spontaneous polarization (P_s) FLC materials. In the present investigation, a very thick cell (∼40 μm) was prepared almost 15 times larger than the pitch value of the material to avoid the surface effect phenomena in the dielectric properties. Figure 1 shows the dielectric permittivity (ε') and loss tangent as a function of frequency at different probing ac voltages at room temperature. As can be seen in Fig. 1(a), the permittivity at lower applied voltages is low and increases with the increase in ac voltage, particularly for lower frequencies, suggesting that there could be more than one dielectric relaxation process. A similar observation has also been reflected in loss tangent curves [Fig. 1(b)]. The low frequency side losses increase with the increase in ac field. The frequency position of the relaxation process is due to the well known Goldstone mode phenomena and the left-hand humps in the loss tangent are due to unwinding of the helical structure, called p-UHM; although there is no clear-cut peak its presence at the higher probing field is clearly reflected. The contribution of the unwound helical mode near the surface of the substrate increases with the increase in applied ac voltage, suggesting that a large portion of the helicoidal structure near the surface gets unwound which is also reflected in the permittivity curves [Fig. 1(a)]. The other collective dielectric process, the soft mode contribution, is ruled out because of the fact that the tilt angle is rigid at room temperature in the deep Sm-C^* phase. This means that the contribution of the collective dielectric processes far away from the transition temperature of the Sm-C^*−Sm-A^* phase is due to the Goldstone mode and the p-UHM processes in the Sm-C^* phase only.

Figure 2 shows the dielectric permittivity and tanδ versus frequency at different temperatures at an applied ac voltage of 30 mV. As seen in the permittivity curves [Fig 2(a)], the variation in the permittivity is much less, suggesting that there is one dielectric process, called the Goldstone mode. However, very close to the transition temperature in the Sm-A^* phase, the presence of only the soft mode is clearly seen in Fig. 2(b), and appears at a higher frequency than the Goldstone mode. This means that at low applied ac voltage, only two collective modes are seen in the Sm-C^* phase. The dielectric studies at 30 mV (considered as low ac voltage) as a function of temperature suggest that the contribution of p-UHM is almost negligible and the Goldstone mode dominates the dielectric properties.

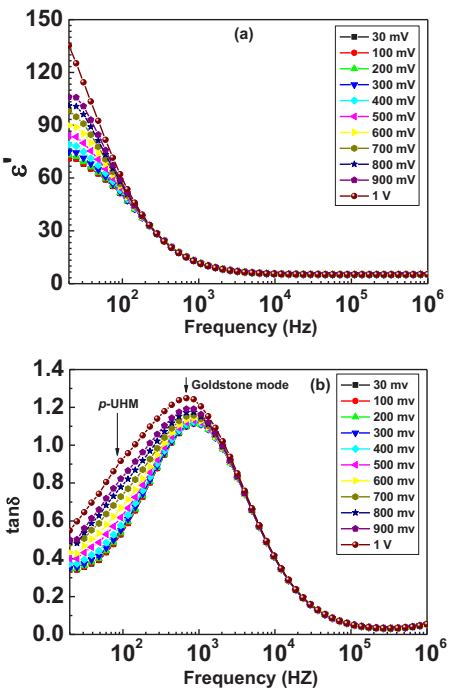

FIG. 1. Dielectric spectroscopy of KCFLC-10S at various probing ac voltages at room temperature, (a) real part (ε') of complex dielectric permittivity, and (b) tanδ versus frequency at various probing ac voltages.

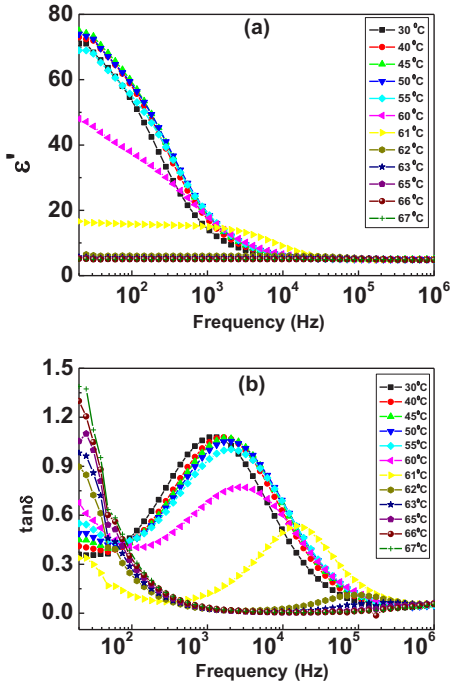

FIG. 2. (a) Real part of complex dielectric permittivity, and (b) tanδ versus frequency at various temperatures, at 30 mV probing ac voltage.

In order to analyze the p-UHM contribution, the amplitude of the probing ac voltage has to be increased beyond the critical voltage. The critical voltage means that the probing ac voltage needed to unwind the helical structure near the surface of the substrates, which is around 500 mV for this material. If the contribution of p-UHM is small in the deep Sm-C^* phase, the same could be seen dominating near the T_c temperature. Figure 3 shows ε' and tanδ graphs at 1 V applied ac voltage (considered as high ac voltage) at different temperatures. If one compares Figs. 2 and 3, the permittivity [Fig. 3(a)] has increased and the tanδ curves show [Fig. 3(b)] the presence of one more dielectric process near the Goldstone mode which is due to p-UHM. The soft mode is seen near the T_c temperature (61 °C). However, the T_c temperature is mentioned as 64.5 °C in the data sheet, but, from our dielectric observation the T_c temperature of the Sm-C^*−Sm-A^* phase is 61 °C, which is expected due to surface effect and cell thickness, as our cells are highly anchored [13-15]. The Goldstone mode, p-UHM, and soft mode processes at higher applied ac voltage are clearly reflected and contribute to higher dielectric permittivity near T_c as seen in Fig. 3(a). It is worth mentioning here that the p-UHM process is more clearly visible at a higher probing ac voltage and at temperatures near T_c, suggesting that the helix becomes more soft or flexible at higher temperature. The p-UHM process is seen at lower temperatures also but merges with the Goldstone mode at higher temperature near T_c, resulting in the broad peak [Fig. 3(b)].

IV. COLLECTIVE DIELECTRIC PROCESSES NEAR T_c TEMPERATURE

The dielectric processes at transition temperature (61 °C) are examined under various applied ac voltages. Three temperatures have been selected in the vicinity of the transition Sm-C^*, T_c, and Sm-A^* phases to see the behavior of the collective dielectric processes. Figure 4 shows the permittivity

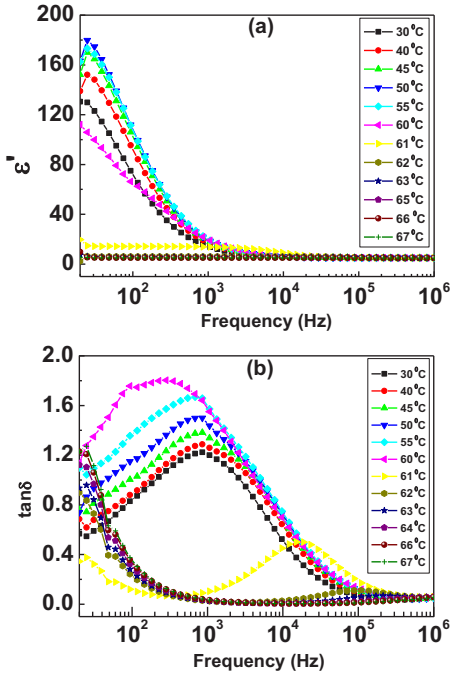

FIG. 3. (a) Real part of complex dielectric permittivity, and (b) tanδ versus frequency at various temperatures, at 1 V probing ac voltage.

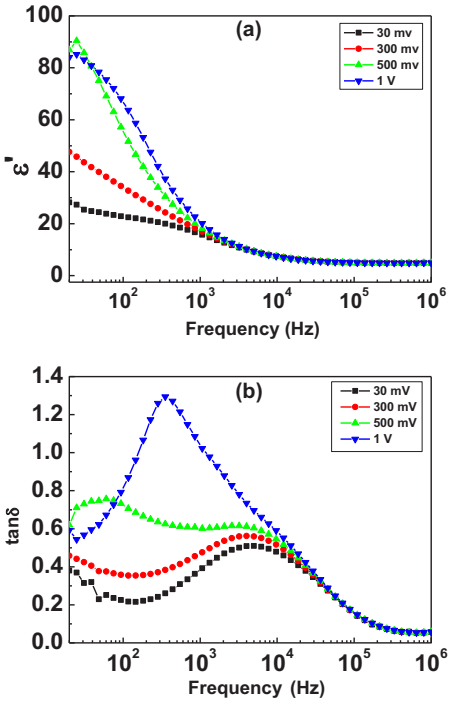

FIG. 4. (a) Real part of complex dielectric permittivity, and (b) tanδ versus frequency at various probing ac voltages at 60.7 °C.

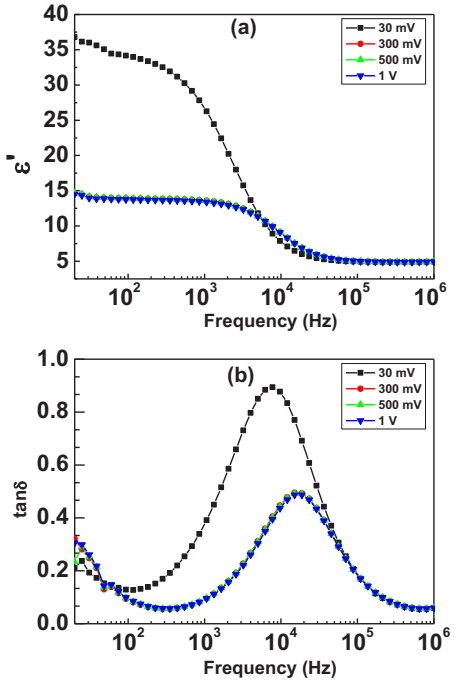

FIG. 5. (a) Real part of complex dielectric permittivity, and (b) tanδ versus frequency at various probing ac voltages at 61 °C.

and tanδ at 60.7 °C (just 0.3 °C below T_c) at different probing ac voltages. The ε' is around 25 at 30 mV ac voltage and then it increases to 85 at 1 V. If one sees the tanδ versus frequency graph [Fig. 4(b)], at low applied field only one peak appears due to the Goldstone mode. As the applied field is increased, the low frequency peak starts appearing which is due to the p-UHM process and at 1 V, the low frequency mode overcomes the Goldstone mode [Fig. 4(b)]. This means the permittivity due to the p-UHM process dominates the Goldstone mode and increases almost three times as seen in Fig. 4(a).

The dielectric processes occur exactly at the transition temperature of the Sm-C^* to Sm-A^* phase at 61 °C, where the material goes from the ferro- to the paraelectric phase and the C_2 *symmetry is changed to cylindrical symmetry* in the Sm-A^* phase. If one sees the dielectric permittivity at T_c for low ac voltage (30 mV) [Fig. 5(a)], ε' is high (∼35) and as ac voltage is increased to 300 mV, the ε' drops to ∼15. The permittivity remains the same with even further increase in the ac voltage up to 1 V, as shown in Fig. 5(a), suggesting the high dependence of ε' on ac voltage. If one sees the relaxation peak at 30 mV, it appears to be due to the Goldstone mode around 3 kHz and as the voltage increases to 300 mV, the relaxation frequency jumps to 10 kHz, suggesting that it is due to the soft mode as shown in Fig. 5(b). Now the question arises of whether the relaxation peak at very low ac voltage (30 mV) is due to the Goldstone mode or to the p-UHM process. This aspect will be further analyzed by applying a bias field in the next section. Figure 6 shows the dielectric permittivity and tanδ as a function of frequency at 61.3 °C at different ac voltages. The permittivity is very low [Fig. 6] and relaxation frequency is the same at all ac voltages [inset of Fig. 6], suggesting that this phase is completely in the Sm-A^* phase and the dielectric process is only due to soft mode phenomena; hence, there is

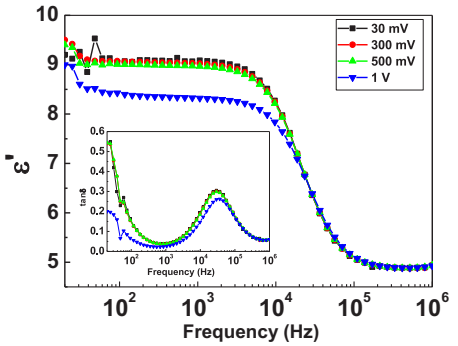

FIG. 6. Real part of complex dielectric permittivity and (inset) tanδ versus frequency at various probing ac voltages at 61.3 °C.

no contribution of the p-UHM and Goldstone modes, as the nature of the soft mode is weakly dependent on field.

Now we analyse the dielectric process at T_c and 1 °C below T_c for low and high ac voltages. Figure 7(a) shows dielectric permittivity at 30 mV ac voltage at 60 °C and 61 °C. As seen in the figure, there is no change in the ε' values and they almost remain the same (∼50) for both temperatures. If one sees the relaxation frequency peaks in the curves [inset of Fig. 7(a)] at these two temperatures, it is almost the same around 2–3 kHz. When the ac voltage is increased to 1 V [Fig. 7(b)], the permittivity at 60 °C in the Sm-C^* phase increases to 120, and at 61 °C (T_c) it decreases to 25, whereas the relaxation frequency at 60 °C is at a low frequency around 300 Hz which is clearly due to the p-UHM process. At 61 °C, the relaxation

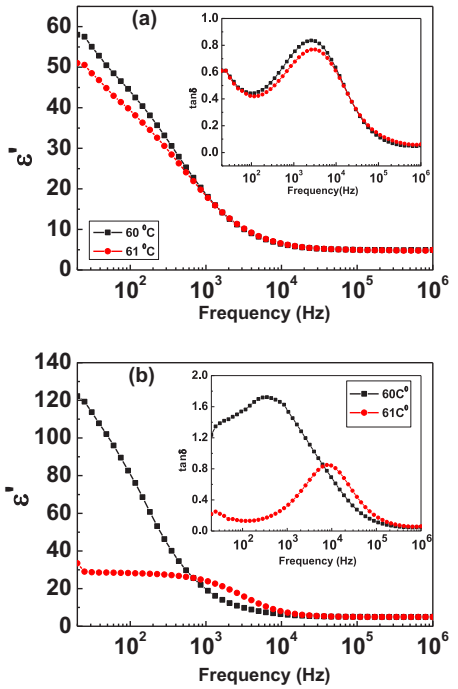

FIG. 7. (a) Real part of complex dielectric permittivity and (inset) tanδ versus frequency at 30 mV probing ac voltage, and (b) real part of complex dielectric permittivity and (inset) tanδ versus frequency at 1 V probing ac voltage in Sm-C^* (60 °C) and at T_c (61 °C) of the Sm-C^*−Sm-A^* phase.

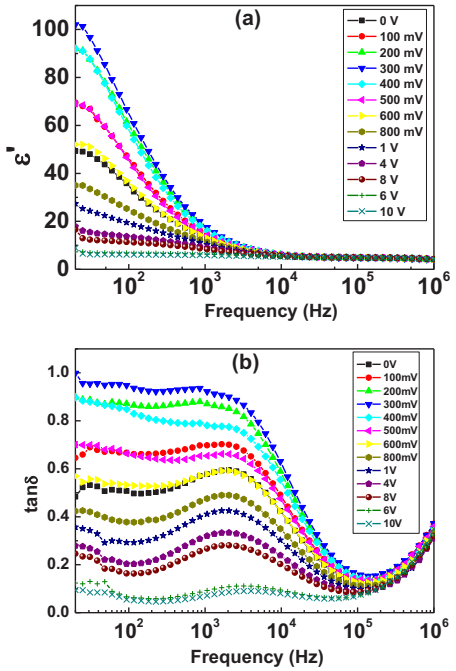

FIG. 8. (a) Real part of complex dielectric permittivity and (b) tanδ versus frequency at various dc biases at 700 mV probing ac voltage (57 °C).

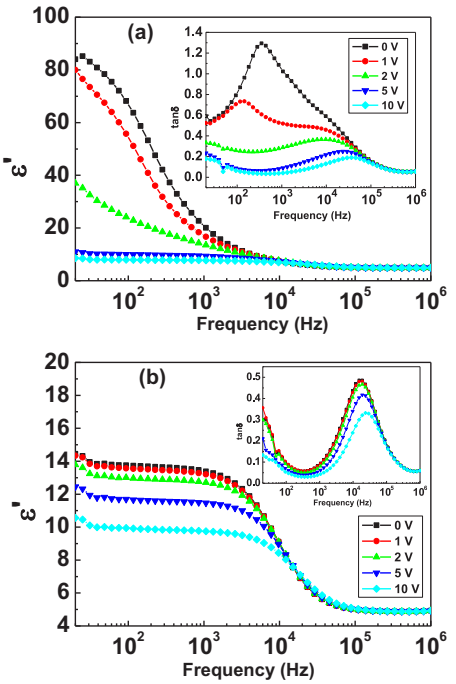

FIG. 9. (a) Real part of complex dielectric permittivity and (inset) tanδ versus frequency at 60.7 °C, and (b) real part of complex dielectric permittivity and (inset) tanδ versus frequency at T_c (61 °C) at 1 V probing ac voltage at various dc bias voltages.

frequency jumps to 10 kHz which is due to the soft mode. The Goldstone mode is also there at 60 °C but is masked by the low frequency p-UHM process [inset of Fig. 7(b)]. However, for the p-UHM and soft mode, a high ac amplitude field is required. This is because the tilt (soft mode) fluctuations are due to the parallel dipole component of the molecule, whereas the Goldstone mode and p-UHM are related to phase fluctuations and helical structure, respectively. This means that we are able to see three collective dielectric processes close to the transition temperature and at T_c in the Sm-C^* phase of the FLC material.

V. EFFECT OF dc BIAS FIELD

The effect of a dc bias field on collective dielectric processes has been studied in the vicinity of T_c. To isolate the soft mode process, the measurements were conducted almost 4 °C below the T_c temperature (57 °C). Figure 8(a) shows permittivity at different dc biases at a probing ac voltage of 700 mV. As seen in the figure, the permittivity at zero bias voltage is around 50 at low frequency. As the bias voltage is increased to 300 mV, the permittivity is also increased up to 100. It is surprising to see that as the bias field increases, the permittivity first increases and then continuously decreases. This is due to the fact that the helix gets unwound and contributes to the increase in the dielectric permittivity, which means that p-UHM process has a definite threshold field depending upon the thickness of the cell. The p-UHM process gets suppressed once the threshold (300 mV for this temperature) is crossed as seen in Fig. 8(a). As shown in Fig. 8(b), the behavior of tanδ versus frequency is similar. It should be emphasized here that the curves are not sharp because of the fact that the relaxation frequencies of the Goldstone mode and the p-UHM process are close to each other and their amplitudes are almost the same, so it is difficult to resolve the two relaxation processes. Since the cell thickness is large (~40 μm), the threshold field for p-UHM is also large. This means that there are clearly two collective dielectric processes and both modes get suppressed as the bias field is increased, as shown in Fig. 8(b).

The effect of the dc bias field on the collective dielectric processes has been studied at T_c. Figure 9(a) shows the permittivity and tanδ curve as a function of frequency just 0.3 °C (at 60.7 °C) below T_c at 1 V ac voltage at different dc bias voltages. The permittivity is very high at a dc bias of 1 V, suggesting that the Goldstone mode and p-UHM are not suppressed; a clear peak due to p-UHM is seen in the inset of Fig. 9(a). This means that ε' is mostly contributed by the p-UHM process and the Goldstone mode while the soft mode is overlapped by lower frequency dielectric processes. As the bias field is increased, the permittivity drastically decreases [Fig. 9(a)] and at 5 V dc bias, a clear relaxation peak due to the soft mode process is visible at ~25 kHz [inset of Fig. 9(a)], suggesting that all three collective dielectric processes are seen in the Sm-C^* phase very close to T_c. Figure 9(b) shows the permittivity and tanδ curve versus frequency at exactly the T_c temperature (61 °C) for the ac voltage of 1 V at different dc bias voltages. As seen in Fig. 9(b), the permittivity is already low, ~14, and the peak at zero bias fields could be due to the soft mode process around 10 kHz [inset of Fig. 9(b)]. When the bias is increased the permittivity due to the soft mode process decreases and the relaxation frequency slightly increases which is well known and reported in the literature; also the soft mode is weakly bias dependent [16]. It should be mentioned here that at low voltage (30 mV), the p-UHM and Goldstone processes are clearly detected at T_c [Fig. 7].

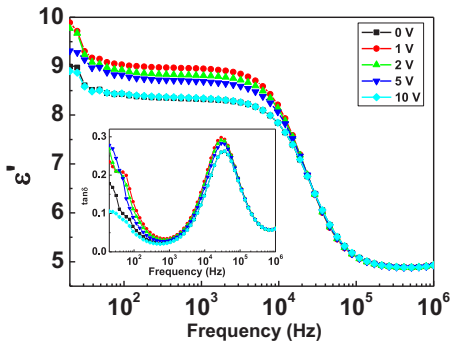

FIG. 10. Real part of complex dielectric permittivity and (inset) tanδ versus frequency at various dc biases at 1 V probing ac voltage in the Sm-A^* phase (61.3 °C).

Figure 10 shows the ε' and tanδ curve versus frequency at just 0.3 °C above the T_c temperature in the Sm-A^* phase. Here the permittivity is already low and with the increase in dc bias field the permittivity gets suppressed marginally and the relaxation peak frequency does not change much as seen in the inset of Fig. 10, which is characteristic of the soft mode. This means that the collective dielectric process in the Sm-A^* phase which is a paraelectric phase is due to tilt fluctuations only and it is well understandable that when one goes from ferroelectric to paraelectric, the C_2 symmetry in the Sm-C^* phase *is changed to cylindrical* symmetry in the Sm-A^* phase; therefore, there cannot be phase fluctuation or a helix related dielectric process in the Sm-A^* phase.

VI. CONCLUSION

The dielectric processes related to helix, phase, and tilt fluctuations have been studied. Three collective dielectric processes have been observed in the vicinity of the Sm-C^*−Sm-A^* phase transition temperature. The tilt fluctuation is observed close to the transition temperature of the Sm-C^*−Sm-A^* phase only. The helical mode, called the partially unwound helical mode (p-UHM), is observed throughout the Sm-C^* phase which is dependent on an oscillating field and dominates the dielectric permittivity, ε', at high ac voltage in the Sm-C^* phase. The Goldstone mode can be detected at very low probing ac voltages. All the collective dielectric processes contribute to the dielectric permittivity near the T_c temperature in the Sm-C^* phase. The Goldstone mode and p-UHM are highly bias dependent, whereas the soft mode is weakly bias dependent in FLC materials.

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