pISSN: 2321 – 9742

The Sapience

Advances in Physical Science Research

Dielectric Studies of the Soft Mode and Goldstone Mode in Twist Grain Boundary Phases

Manisha Chaudhry[1*], Anjuli Khandelwal[2], S. S. Bawa[3]

[1*]Department of Physics, JSSATE, Noida, 201301, UP, India
[2]Department of Physics, S.D. (PG) College, Muzaffarnagar, 251001, UP, India
[3]Polymeric and Soft Material Section, National Physical Laboratory, New Delhi, India
*E-mail: dr.manishachaudhry@gmail.com

Abstract

Dielectric studies are performed on twist grain boundary phases in the frequency range 100 Hz to 1 MHz at different temperatures and bias. The sample investigated shows TGBC*-TGBA*--N*- BP- I phase sequence. The dielectric measurements are performed near the transition TGBA*-TGBC*.

Without DC bias, the dielectric absorption spectra indicates one relaxation process for the TGBC* phase and two relaxation processes for the TGBA* phase. The TGBC* relaxation process could be attributed to the Goldstone mode. The dielectric behavior of the TGBC* phase is completely different with and without bias. The Goldstone mode is strongly attenuated at high DC bias near the transition TGBA*-TGBC*. This is well explained by two distinct orientations of the helical axis-perpendicular to the sample without bias and parallel under bias. The relaxation frequency is found to increase with temperature and decrease with the increase in bias. At sufficiently high bias the relaxation frequency for the Goldstone mode is found to remain constant with temperature well in the TGBC* phase.

The dielectric spectra for the TGBA* phase in the absence of the direct bias voltage exhibits two relaxation processes. These are assigned as the soft mode and the molecular relaxation process in the grain boundaries (PGB). The effect of direct bias voltage on the dielectric response of the TGBA* phase is different from the SmA phase in that the relaxation frequency of the soft mode decreases instead of increasing with increase in bias voltage.

Keywords: Liquid Crystals, TGB, Dielectric spectra, Goldstone mode, Grain Boundaries.

1. Introduction

Chirality gives rise to a rich variety of modulated equilibrium phases in liquid crystals including the cholesteric, smectic C*, Twist Grain Boundary Phases (TGB) and blue phases. TGB phases have attracted to a lot of attention in recent years. The twist grain boundary (TGB) phases are fascinating defect states of chiral smectic liquid crystals whose basic structure comprises a helically twisted stack of ordinary smectic-A, C or C* slabs connected by two-dimensional walls of screw dislocations ("grain boundaries") [de Gennes (1972), Renn (1988) and Renn (1992]. These phases are analogous to the Abrikosov's triangular flux vortex lattice which occurs in type II superconductors in an externally imposed magnetic field. Like Abrikosov's flux lattice, the TGB would occur if $K \equiv \lambda/\xi$, the ratio of the twist penetration depth divided by the smectic coherence length, exceeded $1/\sqrt{2}$.

Temperature dependent dielectric spectroscopy is an important tool to detect weak transitions of the liquid crystal mesophases. The dielectric studies on TGB phases are few [Bougrioua (1996), Pandey (2007), Gupta (2005), Dhar (2003), Girold (1993) and Nguyen (1993)]. The dielectric studies on TGB phases show that in TGBA and TGBC phases, like in the SmA and SmC* phases, the electric field induces amplitude fluctuations of the tilt angle (soft mode) and also the phase fluctuation (Goldstone mode) [Parneix (1988) and Gouda (1991)]. Wrobel et al. [Wrobel (1995)] showed that in the TGBA phase, soft mode relaxation process behavior differs from that anticipated by the extended mean-field theory. Xu et al. [Xu (1995)] showed the existence of the soft mode in the TGBA phase and highlighted the existence of a low frequency mode assigned to the relaxation process in the grain boundaries. M. Ismaili [Ismaili (2001)] highlighted the dielectric behavior differences between TGBA and TGBC phases and put into evidence the influence of the block structure. The TGB phase relaxation processes are found to have lower amplitudes and higher frequencies in comparison with those of classical SmA and SmC phases.

2. Experimental

Different mesophase transition temperatures were determined by using a Differential Scanning Calorimeter (DSC) of Mettler Toledo (Model DSC822^e with STAR^e software). DSC thermograms were located with an accuracy of ± 0.2^{o}C whereas the temperature reproducibility of the measurements was better than ± 0.1^{o}C.

A transmitted light polarizing microscope, OLYMPUS BX 51P was used to identify the textures of different mesophases. The cell thickness was 6μm.

Dielectric permittivity was measured in cells of the sandwich type. Highly conducting ITO coated glass plates were used as electrodes, which allow us to check optical alignment of the liquid crystal molecules. One of the electrodes was pretreated with adhesion promoter and nylon and unidirectional rubbed. Thickness of the cells was controlled by using thin mylar spacers of known thickness (6μm). The cells were first calibrated using air and toluene as standard references. This calibration allows us to calculate absolute values of the dielectric permittivity.

The material was introduced by means of capillary action at elevated temperature in the cells. A well-aligned sample is obtained by applying an electric field in slow cooling cycle and simultaneously observing it under polarizing microscope. The temperature stability was maintained at ± 0.1 ^{o}C by INSTEC STC 200 temperature controller. Measurements were carried out using HP 4192A impedance analyzer in the frequency range of 100 Hz to 1 MHz. The dielectric measurements were computer controlled and automated.

3. Results and Discussion

3.1. Thermodynamic and Optical Investigations

Binary mixtures of different weight proportions of Cholesteric Nonanoate (CN) and N- (4 – Ethoxy benzylidine)- 4 - butyl aniline (EBBA) are prepared these mixtures show variety of Twist grain boundary phases. The mixture CN 30 [70 % CN and 30 % EBBA] show room temperature TGBC* phase.

The mixture exhibits the following polymorphism

$$\text{SmA} \xrightarrow[12.0\ \text{J/gm}]{26.6\ ^{o}\text{C}} \text{TGBC*} \xrightarrow[38.4\ \text{mJ/gm}]{44.7\ ^{o}\text{C}} \text{TGBA*} \xrightarrow[0.9\ \text{J/gm}]{54.7\ ^{o}\text{C}} \text{N*} \xrightarrow[1.3\ \text{J/gm}]{75.8\ ^{o}\text{C}} \text{I}$$

Figure 1a shows cylindrical and cone (CC) type texture with radial streaks originating from the eyes of the CC domains at the transition N*-TGBA. In this texture along with cylindrical and cone like domain texture (similar to that observed for columnar phases) one can clearly see several radial streaks originating from the eye of the CC domains. Figures 1b and 1c show well-developed CC type texture in TGBA* phase at two different temperatures. This texture is similar to the textures recorded by Ribeiro et.al. [Ribeiro (2000)] for TGBA* phases. TGBA* phase transforms to TGBC* phase at 36 ^{o}C (figure 1d). In the TGBC* phase, the CC domains are decorated with fracture lines. These lines appear very faint first and get more and more visible on decreasing temperature. They seem to approach a point as the temperature is lowered. This point seems to correspond to a χ- line (edge dislocation line in the cholesteric ordering, or unwinding line) roughly perpendicular to the preparation. It appears that the helix is unwinding as the temperature is decreased.

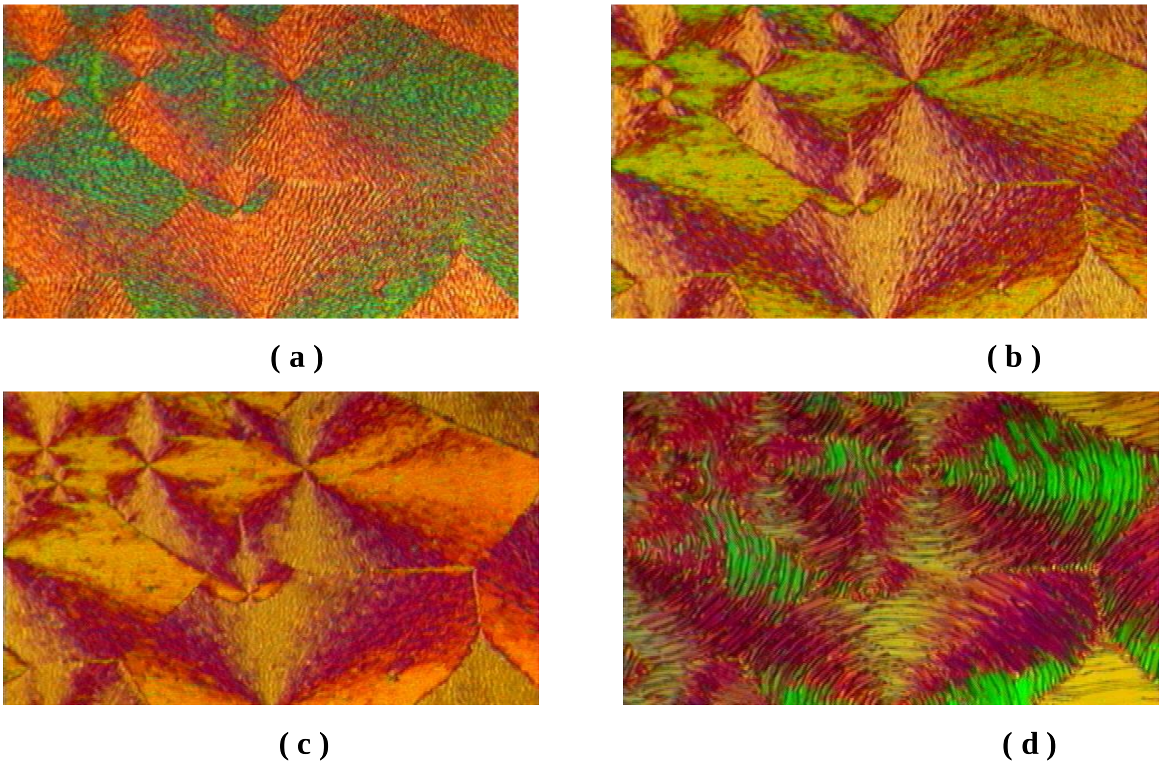

Figure 1: (a) N* -TGBA transition, b) CC type texture with radial streaks originating from the eyes of the CC domains in TGBA phase, (c) Well grown CC type domains in TGBA* phase, (d) TGBC* phase with fracture lines

3.2. Dielectric Absorption Curve at Different Frequencies at Zero Bias

Dielectric measurements as a function of temperature are carried out during the cooling cycle starting from the isotropic phase. The dielectric absorption ε'' as a function of frequency at different temperatures at zero bias is shown in Figure 2. In the TGBC* phases, the relaxation process centered in the lower frequency range at 10^3 Hz is assigned to the Goldstone mode. In the TGBA* phase two relaxation processes are observed. The relaxation process centered in the higher frequency region at 10^4 - 10^5 Hz is assigned to the collective mode. This is caused by the fluctuation in the magnitude of the molecular director (soft mode). The second relaxation process that is being observed in the frequency region (10^3 – 10^4 Hz) is assigned to the process in grain boundary (PGB) as explained earlier by Xu et al. [Xu (1995)]. This process arises from the molecules restricted to lie in the grain boundaries; the latter are responsible for stabilizing the helical structure.

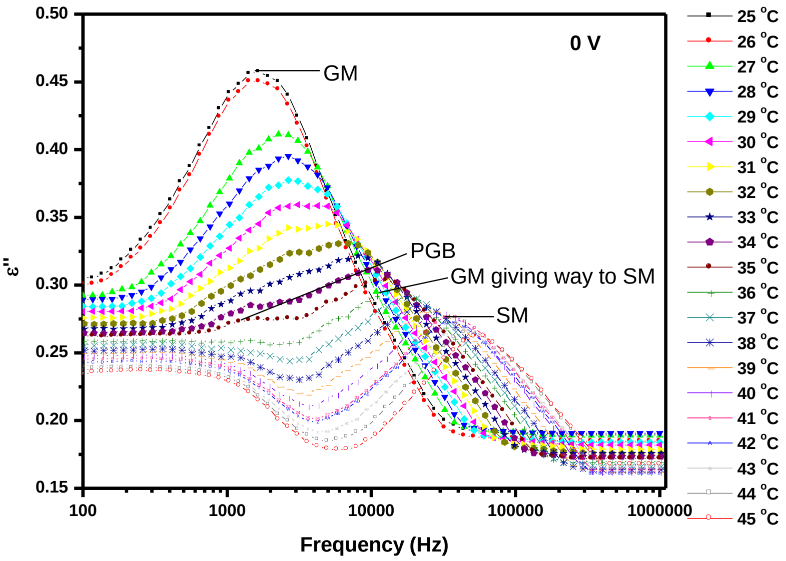

Figure 2: Dielectric absorption ε'' as a function of frequency at different temperatures in TGBC* and TGBA* phases under no bias.

In order to identify the molecular origin of the PGB, Xu et al. [Xu (1995)] considered the packing arrangement of molecules in the grain boundaries. The grain boundaries consist of screw dislocations packed in a manner such that the molecular directors are tilted from the layer normal at a certain angle. Under the applied electric filed, these molecules are likely to contribute to the total dielectric response. The structural studies of TGBA* phase by Srajer et al. [Srajer (1990)] have shown that the ratio of volume of grain boundaries to that of the smectic blocks works out to be less than 20%. Since the dielectric strength is dependent on the number of molecules involved in the relaxation process, hence a relatively weak strength can be expected for the molecules that are restricted to the region of the grain boundaries.

Figure 3 shows the relaxation frequency at different temperatures in TGBC* and TGBA* phases. Both in the TGBC* and TGBA* phase the relaxation frequency is found to increase as the temperature is increased. The slope of relaxation frequency vs. temperature graph is higher for TGBA* phase as compared to TGBC* phase. This may be due to high viscosity of TGBC* phase

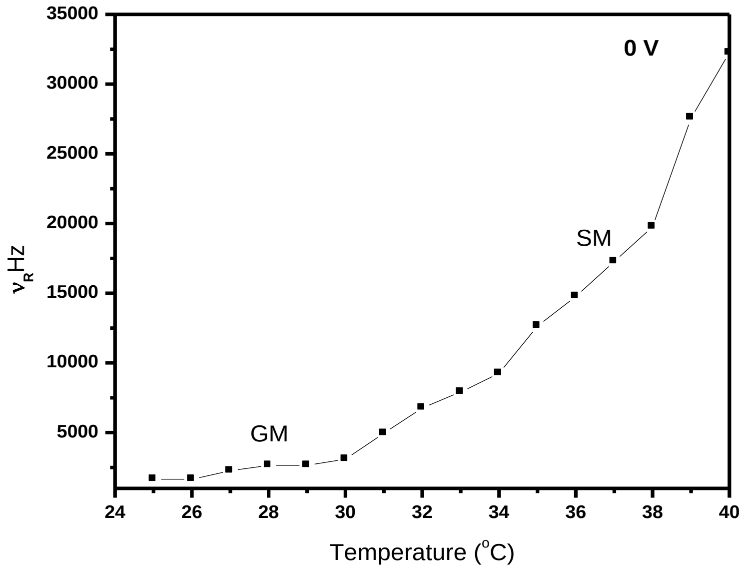

Figure 3: Relaxation frequency at different temperatures in TGBC* and TGBA* phase at zero bias.

3.3. Effect of Bias on the Dielectric Absorption

Figures 4-7 show the dielectric absorption ε″ as a function of frequency at different temperatures under the direct biasing at 1V, 5 V, 10 V and 15 V. The dielectric behavior in the TGBC* phase is strongly modified under the bias. The dielectric absorption ε″ is continuously decreased in the TGBC* and TGBA* with increase of bias.

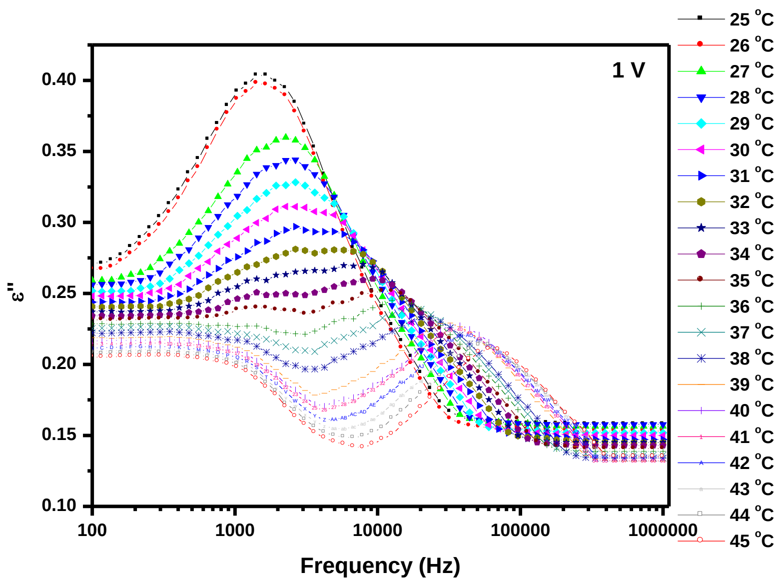

Figure 4: Dielectric absorption ε″ as a function of frequency at different temperatures in TGBC* and TGBA* phases at 1 V.

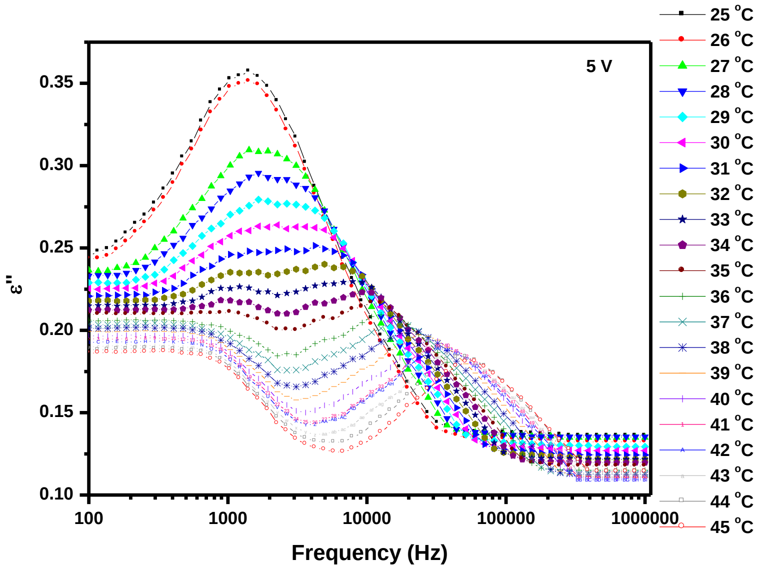

Figure 5: Dielectric absorption ε″ as a function of frequency at different temperatures in TGBC* and TGBA* phases at 5 V.

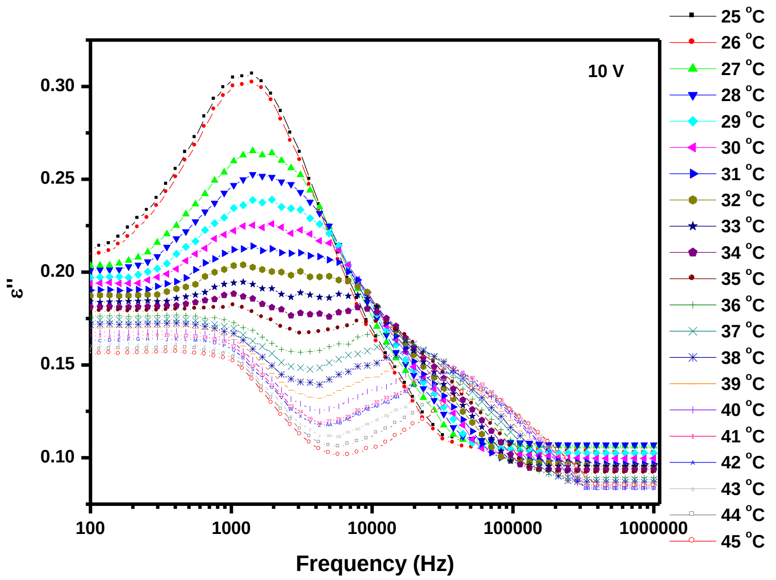

Figure 6: Dielectric absorption ε″ as a function of frequency at different temperatures in TGBC* and TGBA* phases at 10 V.

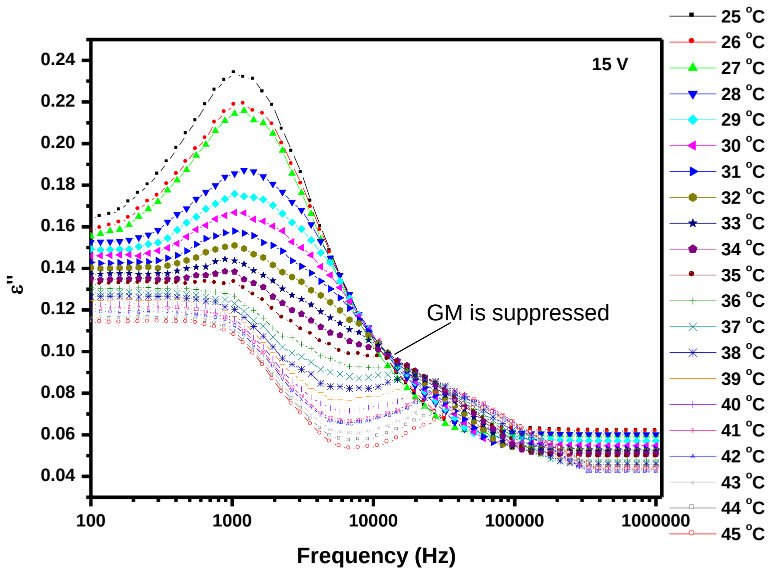

Figure 7: Dielectric absorption ε″ as a function of frequency at different temperatures in TGBC* and TGBA* phases at 15 V.

Figure 8 shows Dielectric absorption curve as the function of frequency at different bias at 27°C in the TGBC* phase. At the Transition TGBC*-TGBA* at 33°C, a new process is found to emerge in the low frequency region at 10^3 Hz (figure 9). For higher bias voltage this relaxation process is pronounced. This may be assigned to the deformation process of the structure because the TGB helix is disturbed by the electric field. During the procedure of forming a perfect SmC* structure by increasing the bias field, the deformation process continues to exist. The process centered at 10^4 Hz is suppressed at 15 V. This mode at Tc is strongly bias field dependent and is considered due to Goldstone mode.

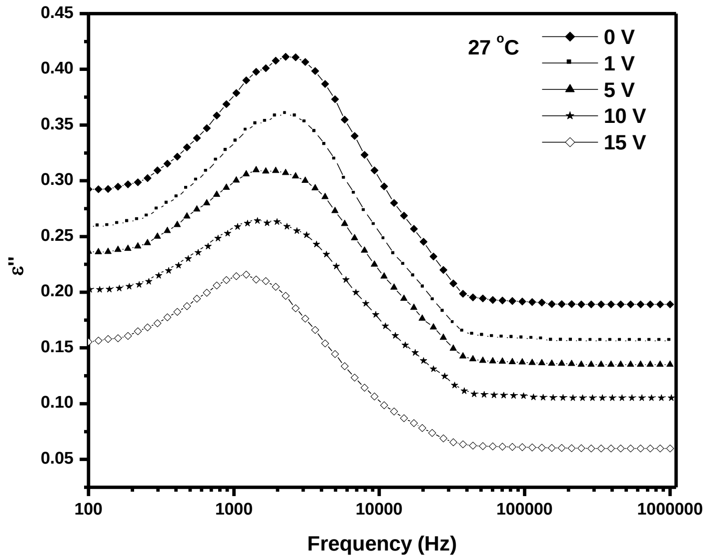

Figure 8: Dielectric absorption ε″ curve as the function of frequency at different bias at 27 ^{o}C in the TGBC* phase.

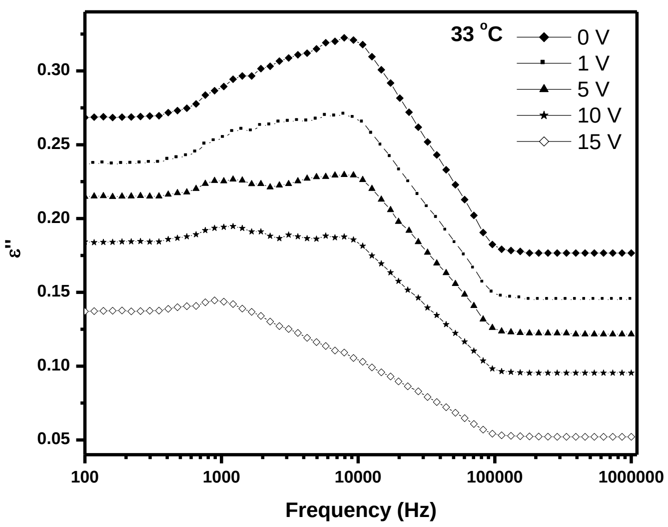

Figure 9: Dielectric absorption ε″ curve as the function of frequency at different bias at 33 ^{o}C at the TGBC*- TGBA* transition.

Figure 10 shows dielectric absorption in the TGBA* phase at 35 ^{o}C. The mode centered at 10^3 Hz could be the PGB and the other at 10^4 Hz is the soft mode. It is clearly seen that the mode centered at 10^4 Hz is not suppressed even at 15 V.

Under 15V bias, the relaxation frequency is found to remain constant till the TGBC* - TGBA* transition (figure 11). At the transition, in the TGBA* phase the relaxation frequency increases sharply. This behavior may correspond to a Sm C* phase that appears due to helical unwinding in TGBC* phase.

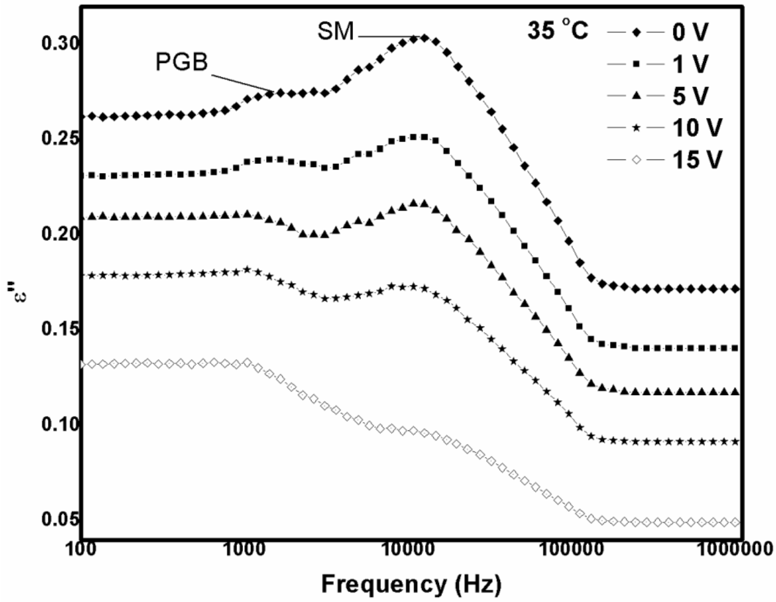

Figure 10: Dielectric absorption ε″ curve as the function of frequency at different bias at 35 °C in the TGBA* phase.

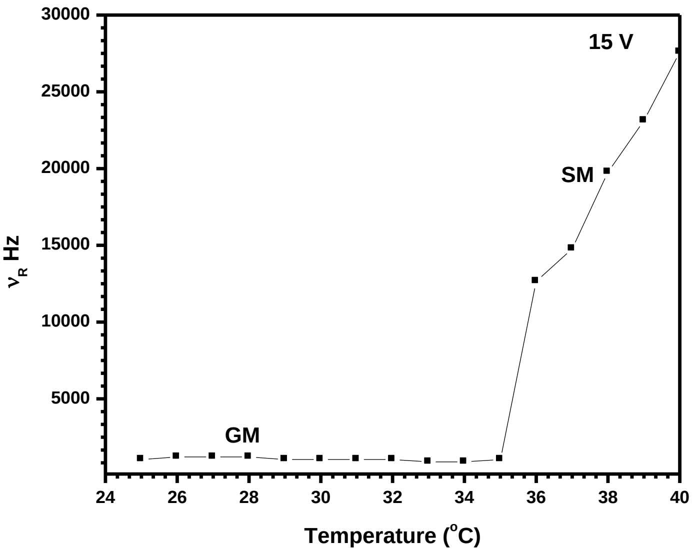

Figure 11: Relaxation frequency at different temperatures in TGBC* and TGBA* phase at 15V

4. Conclusion

The dielectric spectra in the absence of direct bias voltage for the TGBA* phase as a function of temperature exhibits two relaxation processes. These are assigned as (a) the soft mode and (b) the molecular relaxation process in the grain boundaries (PGB).

The effect of direct bias voltages on the soft mode of the TGBA* phase is clearly different from that of the SmA phase. In the TGBA* phase, the relaxation frequency of the soft mode decreases with increasing bias voltages instead of the opposite as in the case for the SmA phase. The relaxation process in the grain boundaries gradually disappears with increasing bias. The later provides evidence that the grain boundaries are gradually destroyed by the electric field.

The effect of direct bias voltage on the dielectric spectra of the TGBC* phase differs from that of the SmC* phase. The relaxation frequency of the Goldstone mode is found to decrease with increase in bias. It may be due to TGB helix unwinding by the electric field. The decrease in relaxation frequency arises from increase in the viscosity of the system to the collective mode.

In the TGBC* phase, for higher bias voltage a relaxation process is found to emerge at low frequencies. This may be assigned to the deformation process of the structure because the TGB helix is disturbed by the electric field. During the procedure of forming a perfect SmC* structure by increasing the bias field, the deformation process continue to exist.

The dielectric behavior of TGBC* phase is completely different with and without bias. At the TGBC*-TGBA* transition, the Goldstone mode is cancelled or strongly attenuated. This is explained by two distinct orientation of the helical axis: perpendicular to the sample without bias and parallel under bias. In the first case, the active component of the field is always perpendicular to the polarization. In the second case it is mainly parallel.

Under 15V bias, the relaxation frequency is found to remain constant till the TGBC* - TGBA* transition. This behavior corresponds to a Sm C* phase that appears due to helical unwinding in TGBC* phase.

5. Acknowledgment

I am thankful to Dr. Vikram Kumar, Director, National Physical Laboratory, New Delhi, for extending all facilities to pursue this work. I am sincerely grateful to Dr. A. K. Gupta, Sc. ‘G’ Head of Engineering Material Division for his encouragement.

I express my sincere and deepest gratitude to Dr. A. M. Biradar, Sc. 'F', who encouraged me in every conceivable manner through his needful help, wholehearted co-operation and valuable guidance.

5. References

1. Bougrioua, F., N. Isaert, C. Legrand, A. Bouchta, P. Barois and H. T. Nguyen, 1996. Dielectric properties of TGBA and TGBC phases. Ferroelectrics, 180: 35-48.
2. de Gennes, P. G., (1972). An Analogy between Superconductors and Smectics-A. Solid St. Commun., 10: 753-756.
3. Dhar, R., A.K. Srivastava and V.K. Agarwal, (2003). Induced twisted-grain-boundary phases in the binary mixtures of a cholesteric and a nematic compound. Phase Transitions, 76: 959-974.
4. Girold, C., C. Legrand, N. Isaert, P. Pochat, J. P. Parneix, H. T. Nguyen and C. Destrade, (1993). Dielectric investigation of the helical smectic A* (TGBA) - SC* phase transition. Ferroelectrics, 147: 171-179.
5. Gouda, F., K. Skarp and S. T. Lagerwall, (1991). Dielectric studies of the soft mode and Goldstone mode in ferroelectric liquid crystals. Ferroelectrics, 113: 165-206.
6. Gupta, M., R. Dhar, V.K. Agarwal, R. Dabrowski and M. Tykarska, (2005). Dielectric spectroscopy of a binary mixture of liquid crystals showing wide temperature range twisted grain boundary phase with re-entrant cholesteric phase. Phy. Rev. E, 72: 021073.
7. Ismaili, M., F. Bougrioua, N. Isaert, C. Legrand and H. T. Nguyen, (2001). Influence of the Dielectric properties of twist grain boundary phases: anchoring and the distance between grain boundaries. Phy. Rev. E, 65: 11701-11715.
8. Nguyen, H. T., C. Destrade, J. P. Parneix, P. Pochat, N. Isaert and C. Girold, (1993). TGBA phase in chiral two ring derivatives. Ferroelectrics, 147: 181-191.
9. Pandey, M.B., R. Dhar, A.S. Achalkumar and C.V. Yelamggad, (2007). Characteristic dielectric behaviour of the wide temperature range twist grain boundary phases of unsymmetrical liquid crystal dimmers. J. Phys. Condens. Matter, 19: 436219.
10. Parneix, J. P. and C. Legrand, (1988). Dielectric properties of ferroelectric liquid crystals. Ferroelectrics, 84: 199-207.
11. Renn, S. R. and T. C.Lubensky, (1988). Abrikosov dislocation lattice in a model of the cholesteric–to–smectic-A transition. Phys. Rev. A, 38: 2132-2147.
12. Renn, S. R., (1992). Multicritical behavior of Abrikosov vortex lattices near the cholesteric–smectic-A–smectic-C* point. Phys. Rev. A, 45: 953-973.
13. Ribiero, A. C., H. T. Nguyen, Y. Galerne and D. Guillon, (2000). Optical textures in TGBA mesophases. Liq. Cryst., 27: 27-34.
14. Srajer, C., R. Pindak, M. A. Waugh and J. W. Goodby, (1990). Structural measurements on the liquid-crystal analog of the Abrikosov phase. Phys. Rev. Lett., 64, 1545-1548.
15. Wrobel, S., S. Hiller, M. Pfeiffer, M. Marzec and W. Haase, (1995). Collective and molecular processes in a new class of ferroelectric liquid crystals. Liq. Cryst., 18: 21-29.
16. Xu, H., P. Panarin, J. K. Vij, A. J. Seed, M. Hird and J.W. Goodby, (1995). Investigation of the TGBA* phase in a ferroelectric liquid crystal using dielectric spectroscopy. J. Phy. Condens. Matter, 7: 7443.