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1995 J. Phys.: Condens. Matter 7 7443

(http://iopscience.iop.org/0953-8984/7/38/004)

J. Phys.: Condens. Matter 7 (1995) 7443–7452. Printed in the UK

Investigation of the TGBA* phase in a ferroelectric liquid crystal using dielectric spectroscopy

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Received 31 May 1995

Abstract. The dielectric response of a ferroelectric liquid crystal with the TGBA* phase has been investigated over the frequency range 0.1–10^6 Hz. The dielectric properties as a function of temperature and direct bias voltages of the TGBA* phase exhibit behaviour different from that in the smectic A (SmA) phase. From the dielectric spectra, two relaxation processes, instead of only one process (the soft mode) previously known, have been found for the helical TGBA* phase in the absence of the direct bias voltage. These are assigned to (a) the soft mode and (b) a relaxation process in the grain boundaries. The latter process is found for the first time. The dielectric response for the SmC*–TGBA* transition suggests a weakly first-order phase transition. The effect of direct bias voltage on the dielectric spectra of the TGBA* phase differs from that of the SmA phase in terms of (a) the relaxation frequency of the soft mode decreases instead of increasing with increase in the bias voltage—suggested to arise because the TGB helix is unwound by the electric field, and (b) a relaxation process is found to emerge for higher bias voltages. The latter is assigned to the deformation process of the structure because the TGB helix is disturbed by the electric field.

1. Introduction

The TGBA* phase is an intermediate phase formed during the transition from the cholestric phase to the chiral smectic A (SmA) phase. A molecular packing model for this phase was predicted by Renn and Lubensky [1] and first experimentally discovered by Goodby *et al* [2]. The model for the TGBA* phase predicts small blocks of molecules with a layered SmA structure separated from each other by the grain boundaries of screw dislocations. The layer normal of each block rotates helically with the axis of the helix staying parallel to the smectic layers.

Numerous investigations of the TGBA* phase have been made since its discovery. One relaxation process has so far been detected [3, 4] in this phase from the dielectric spectra. This process has been attributed to the in-plane amplitude fluctuation of the molecular director, the so-called soft mode, which may exist in the small blocks of the TGBA* phase. Various measuring techniques have been used to explore the molecular structure of the TGBA* phase. These are the optical Bragg diffraction, optical texture observations, contact method, pitch measurements, nuclear magnetic resonance (NMR) spectroscopy and infrared spectroscopy. The phase transition behaviour from the relevant TGB phase to the smectic C* (SmC*) or SmA phase has been found to be second or weakly first order [4]. Similar

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0953-8984/95/387443+10$19.50

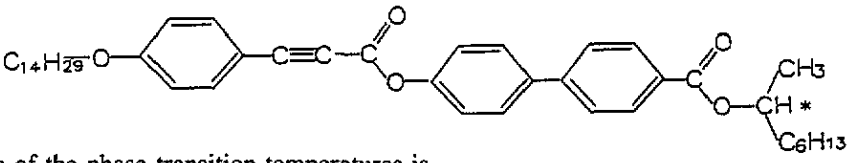
to that of the ferroelectric liquid crystal (FLC) cell with surface-stabilized geometry, the TGB helix was found to be completely suppressed by the cell surfaces [5, 6]. This is due to the surface anchoring effect and a relatively large value of the pitch (0.38–0.63 μm) of the TGB helix. Recently, Shao *et al* [7] observed an irreversible conversion from the helical TGB phase to the normal SmA or SmC* states, which is induced by the electric field. They found the threshold voltage for the 5 μm spacing cell to be within 10–50 V, depending on the temperature. The phenomenon of electric-field-induced transition behaviour in FLCs could have applications in creating laser-addressed LC display devices.

In spite of a considerable interest in the TGBA* phase over the past 5 years, the complicated molecular structure and the physical properties of this phase need to be clarified further. In this paper, we report investigations of the dielectric properties of the TGBA* phase as a function of temperature and the DC bias field, over a frequency range 0.1–10^6 Hz. The aim of this paper is firstly to determine the mechanism of the various relaxation processes in the TGBA* phase and secondly to check whether the dielectric behaviour of the TGBA* phase is similar to that of SmA phase. In particular, we determine the effect of the DC bias field on the dielectric properties of the TGBA* phase.

2. Experimental details

2.1. Ferroelectric liquid crystal material

FLC material AS425 is used for these investigations. Its chemical structure is as follows:



The sequence of the phase transition temperatures is

$$C_r\text{–}80.3\ ^\circ\text{C–}S_c^*\text{–}91.3\ ^\circ\text{C–}S_{c\alpha}^*\text{–}91.3\ ^\circ\text{C–TGBA*–}95.6\ ^\circ\text{C–I}$$

(48.2 °C–Sc*Ferri–39.5 °C–Sc*Anti)

where the subphases shown in parentheses can be detected only on quenching the material to the temperatures below the crystalline phase C_r.

2.2. Dielectric measurements

Test cells are made up of glass plates which on one side are coated with indium tin oxide (ITO) (resistance, 100 Ω per square). Different cell thicknesses (1.5, 6, 10 and 20 μm) were achieved using Mylar spacers. In order to obtain a homogeneously aligned FLC cell, its inner conducting surfaces were first spin coated with 0.8% poly(vinyl alcohol) solution and were rubbed parallel. The FLC cell was then treated by applying a square-wave voltage during cooling from the isotropic phase to the TGBA* phase. The FLC cell was placed on a hot stage and its temperature was automatically varied. The texture of the FLC cell was simultaneously observed using a polarizing microscope during dielectric measurements. This arrangement is used for studying the sample alignment and for observing any special effect on the texture that may occur during the measurements. The experimental arrangement for the dielectric measurements is shown in figure 1. The direct bias (0–40 V) and alternating

(0.1 V RMS) voltages were applied across the homogeneously aligned cell and thus parallel to the smectic layers. This allowed us to measure the transverse component of the complex dielectric permittivity $\epsilon_\perp$. The dielectric experimental data were fitted to the Havriliak–Negami [8] equation

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\Delta\epsilon}{(1 + (i\omega\tau)^{(1-\alpha)})^\beta}.$$

Thus the dielectric relaxation strength $\Delta\epsilon$ and the relaxation frequency $f_m = 1/2\pi\tau$ were obtained. As the dielectric spectra of the cells above 6 μm cell spacing are similar in behaviour, we mainly report the dielectric results for the cells with thicknesses of 1.5 and 6 μm.

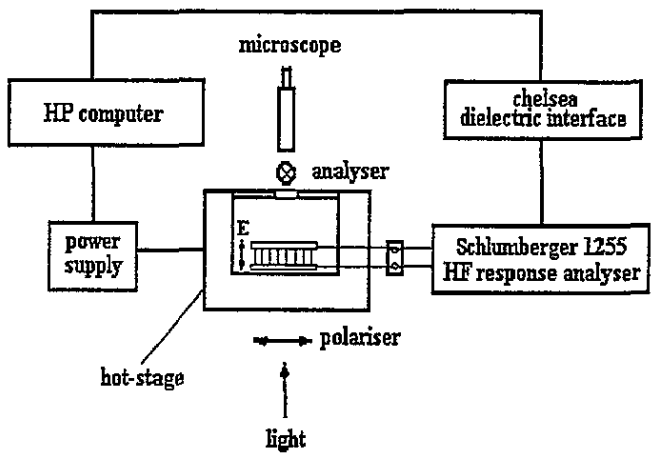


Figure 1. Schematic diagram of the dielectric spectrometer and the polarizing microscopic set-up.

3. Results and discussion

3.1. Observation and assignment of two relaxation processes of the TGBA phase in the absence of a direct bias voltage*

Dielectric measurements as a function of temperature were carried out during the heating cycle starting from the temperature below the crystalline phase C_r. In the TGBA* phase, the dielectric spectra of the cell possessing a helical structure indicate two relaxation processes. These processes are clearly resolved in the Cole–Cole plot (figure 2(a)). The relaxation process with a higher value of the dielectric strength and centred in the higher-frequency region (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). This is confirmed by the dielectric measurements, under a direct bias voltage of 5 V, as a function of temperature. The results for the dielectric strength of this process are shown in figure 3. A divergence of the dielectric strength $\Delta\epsilon$ is observed during the SmC*–TGBA* transition. This confirms that the mode

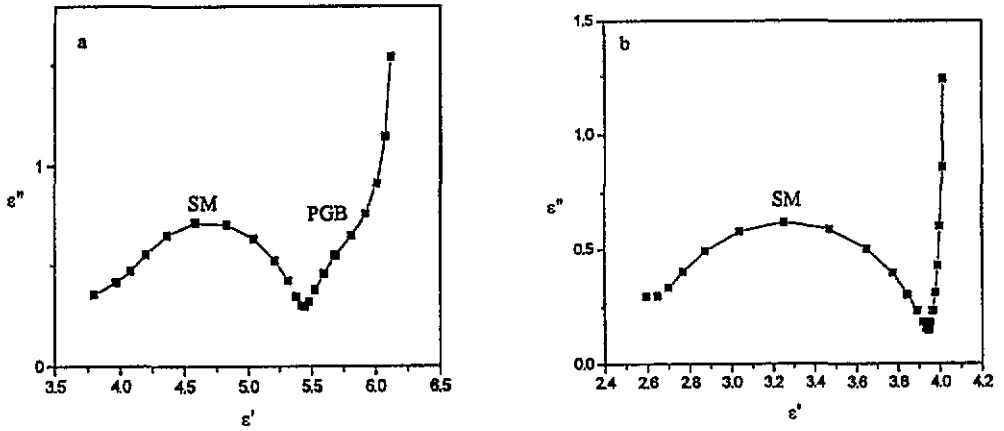


Figure 2. Cole–Cole Plot of the TGBA* phase (92 °C; bias voltage, 0 V) for (a) the 6 μm spacing cell with helical TGB structure and (b) the 1.5 μm spacing cell with TGB helix unwound structure: SM, soft mode; PGB, molecular relaxation process in grain boundaries.

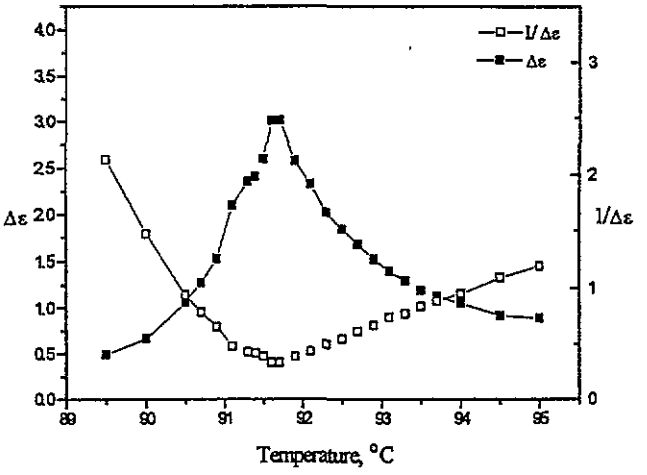


Figure 3. Plots of $\Delta\epsilon$ and $1/\Delta\epsilon$ of the soft mode versus temperature during the heating cycle at a bias voltage of 5 V (6 μm spacing cell).

in question is the soft mode. This relaxation process in TGBA* phase is thus caused by the electroclinic effect.

The second relaxation process that is being observed is centred at a frequency of almost 10^3 Hz. *This to our knowledge is the first observation of a mode through the dielectric* studies of the TGBA* phase [3, 4]. The interesting aspect of these studies is to have found that this relaxation process is detected only in the dielectric spectra of thick cells (above 6 μm), where the helical TGBA* texture was also observed. This relaxation process is found to disappear in the dielectric spectra of a thin cell (1.5 μm) where the TGB helix is suppressed by the surfaces of the cell. These observations strongly suggest that this process arises from molecules restricted to lie in the grain boundaries; the latter are responsible for stabilizing the helical structure of the TGBA* phase. In order to identify the molecular origin of this relaxation process, we consider the packing arrangement of

molecules in the grain boundaries of this phase. The grain boundaries consist of screw dislocations. Molecules in the area of the grain boundaries are packed in a manner such that the molecular directors are tilted from the layer normal at a certain angle. Under the applied electric field, these molecules are likely to contribute to the total dielectric response. The dielectric strength of this relaxation process is relatively weak in comparison to that for the soft mode. Structure studies of the TGBA* phase by Srajer *et al* [9] have shown that the ratio of the volume of the 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. Although the molecules in the grain boundaries are tilted with respect to the layer normal, this relaxation process may not at present be assigned to the Goldstone mode. This is based on the reason that the arrangement of molecules in the grain boundaries is different from that of the SmC* phase; hence the motion of the molecules is not of the same type as in SmC* phase. Further work needs to be carried out to understand the mechanism of this mode. However, this relaxation process can be assigned to the relaxation corresponding to the molecules in the regions of the grain boundaries, referred to as the process in grain boundaries (PGB). Finally, the recent results from NMR spectroscopy obtained by Ferraz *et al* [10] show that the molecular relaxation dispersion in the TGBA* phase is different from that in the normal SmA phase. This was interpreted in terms of a new relaxation process seen in the low-frequency range (less than 10^5 Hz). These observations might correspond to the lower-frequency relaxation process identified in our dielectric spectra.

3.2. Dielectric properties during the SmC–TGBA* phase transition*

The dielectric loss spectra ϵ'' versus frequency, for different temperatures (figure 4), exhibit how the Goldstone mode in SmC* phase changes to the soft mode in the TGBA* phase while the sample is studied from $T < T_c$ up to the TGBA* phase (T_c is the SmC*–TGBA* phase transition temperature). The dielectric relaxation strength $\Delta\epsilon$ and the relaxation frequency f_m as functions of temperature (in the range of interest) are shown in figures 5 and 6 respectively.

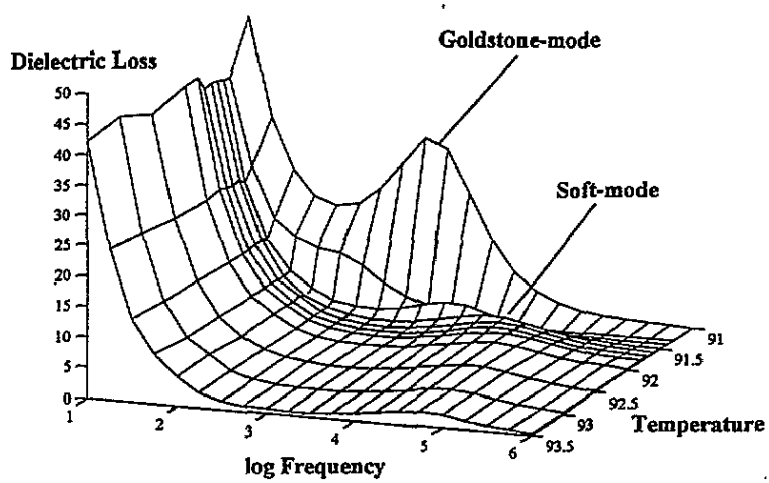


Figure 4. ϵ'' versus frequency at temperatures of 91–93.5 °C for a cell with 6 μm spacing.

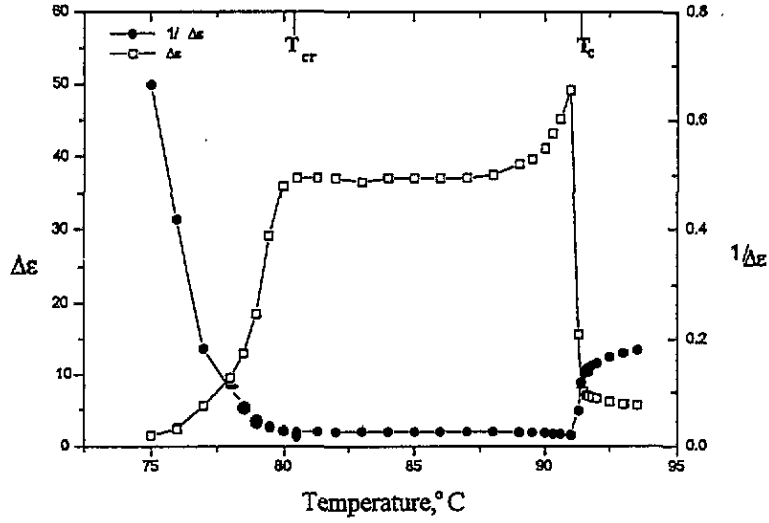


Figure 5. Plots of $\Delta\epsilon$ and $1/\Delta\epsilon$ versus temperature in the temperature range of interest.

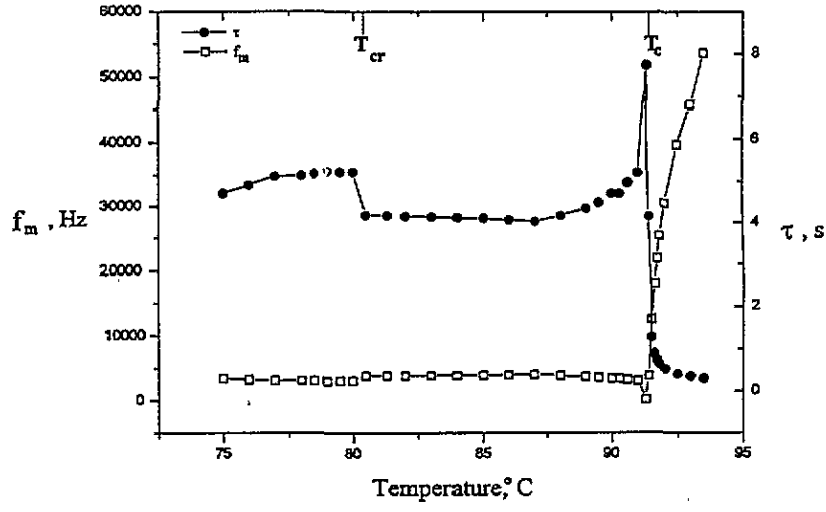


Figure 6. Plots of f_m and τ versus temperature in the temperature range of interest.

Having followed the SmC*–TGBA* phase transition, we find firstly a dramatic decrease in the dielectric strength $\Delta\epsilon$ during the SmC*–TGBA* transition (see figure 5 and secondly that f_m $(= 1/2\pi\tau)$ varies dramatically with temperature at the SmA–TGBA* transition temperature and then away from this temperature the curve flattens off with increasing temperature (figure 6). Similar behaviour is also observed for $1/\Delta\epsilon$ against temperature (see figure 5). These features imply that the SmC*–TGBA* transition is not exactly second order. The pitch measurements made by Nguyen *et al* [4] over the SmC*–TGBA* region clearly show a noticeable divergence of the TGB pitch and of the pitch in the SmC* phase. Based on these measurements, the SmC*–TGBA* transition was found to be weakly first order. An endothermic bump has also been found in the DSC spectra for this transition

in the same sample. Dielectric observations supplement the evidence found from other techniques that the SmC*–TGBA* transition is weakly first order. The existence of the SmC_α phase over a very narrow temperature range between the SmC*–TGBA* phases may be an additional reason for this behaviour.

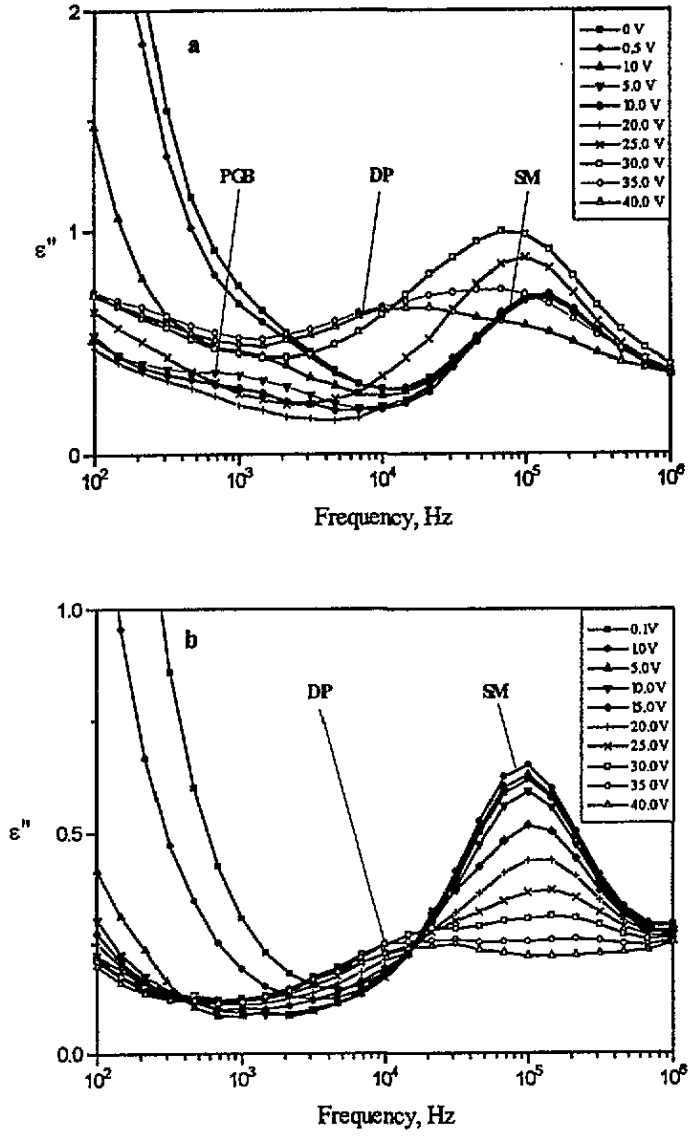


Figure 7. Plot of ϵ'' versus frequency for different bias voltages at a temperature of 92 °C for (a) the 6 μm cell spacing with helical TGB texture and (b) the 1.5 μm cell spacing with TGB helix unwound cell: SM, soft mode; PGB, molecular relaxation process in the grain boundaries; DP, the deformation process. In (a) and (b), the SM and PGB processes are suppressed whereas DP is enhanced, with the increase in the bias voltage except that the PGB process exists only in a thick cell (see figures 8(a) and 8(b)).

3.3. DC bias field dependence of the dielectric properties in the TGBA phase*

The dielectric measurements were carried out by increasing the direct bias voltage for the TGBA* phase. The dielectric loss ϵ'' spectra for a thicker cell (6 μm spacing) are shown in figure 7(a). As found in figure 7(a) the effect of the direct bias voltages on the soft mode of the helical TGBA* phase is clearly different from that of the SmA phase [10, 11]. For the TGBA* phase, the relaxation frequency of the soft mode decreases with increasing bias voltage instead of the opposite as is the case for the SmA phase. Furthermore, a third relaxation process, assigned to the deformation process indicated in figure 7(a) appears on the lower frequency side of the soft mode for bias voltages greater than 20 V. In addition, we find that the relaxation process assigned to molecules in the grain boundaries (PGB) gradually disappears with increasing direct bias voltage. These behaviours can be clearly observed in figure 8(a), which shows the dependence of the dielectric strength for the three relaxation processes (the soft mode, the relaxation process in the grain boundaries and the deformation process) on bias voltage for the cell with helical TGB texture.

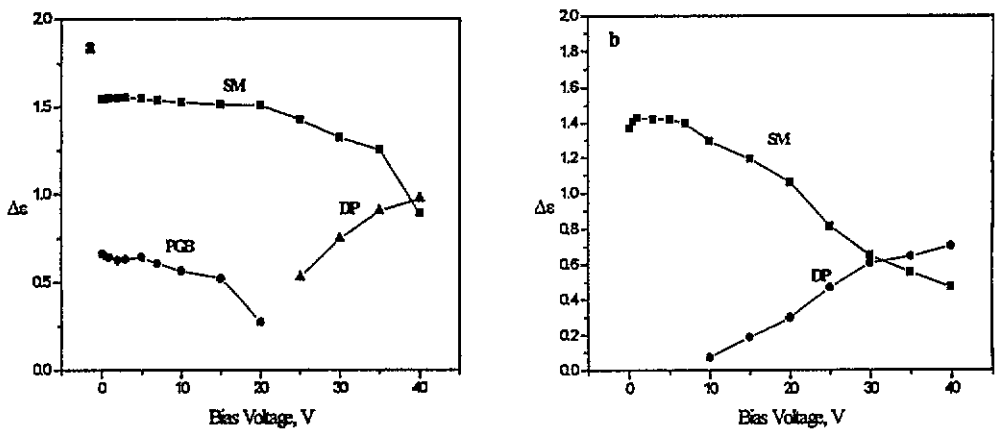


Figure 8. Plot of $\Delta\epsilon$ against bias voltage for various relaxation processes in (a) the 6 μm thick cell with helical TGB texture and (b) the 1.5 μm thin cell with helix unwound texture (SmA texture): SM, soft mode; PGB, molecular relaxation process in grain boundaries; DP, deformation process.

In order to understand the mechanisms that give rise to these experimental observations, we also investigated the dielectric behaviour of a TGB helix unwound cell. Such a helix unwound cell can be obtained using an appropriate cell geometry. In our case, we used a thin cell of 1.5 μm spacing in which the TGB helix is unwound by the surfaces of the cell and the cell exhibits the normal SmA texture. Figure 7(b) shows the bias-dependent dielectric spectra of a thin cell. Figure 8(b) gives the bias voltage dependence of the dielectric strength for the thin cell. The plots of the relaxation frequency of the soft mode as a function of the bias voltage, for a thick cell (6 μm spacing) with helical TGB texture and a thin cell (1.5 μm spacing) with TGB helix unwound texture, are given in figure 9.

Figure 7(b) and 9 show unambiguously that the direct field dependence of the soft mode for the TGB helix unwound cell i.e., a thin cell is different from that of the thick cell, but it is similar to that for the SmA phase [11, 12], where the relaxation frequency increases with increasing bias voltage. However, similar to that for the case of the cell

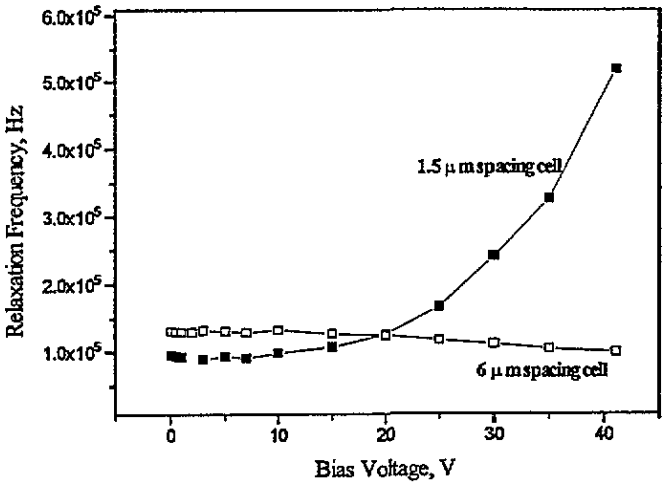


Figure 9. Plot of the relaxation frequency of the soft mode versus the bias voltage for a cell with 1.5 μm spacing (TGBA helix unwound texture or SmA texture) and a cell with 6 μm spacing (helical TGBA texture).

possessing the helical TGB structure (see figure 7(a)), another relaxation process arises for bias voltages above 10 V. The relaxation process is centred at a frequency of almost 10^4 Hz and its amplitude increases with increasing bias voltage. These features are indicated in figures 7(b) and 8(b).

Two questions arise from these findings.

(i) Why is the dielectric response under DC bias field for the cell with TGBA texture different from that of the SmA phase?

(ii) What is the molecular origin of the new relaxation process seen at 10 kHz under high bias voltages?

In an effort to answer question (i), we carefully observed the cell texture during the dielectric measurements. We found that, whenever the relaxation frequency decreased with increasing bias voltage, some small areas with a uniform colour (where the helix starts to unwind) appear. These areas continually keep expanding under high bias voltages. It should be noted that the relaxation process in the grain boundaries gradually disappears with increasing bias voltage. The latter provides evidence that the grain boundaries are gradually destroyed by the electric field. Note that the bias-dependent behaviour of the soft mode in the helix unwound cell is similar to that of the SmA phase. These facts support the following conclusions.

(i) The system with helical TGB structure undergoes a helix unwinding process.

(ii) The decrease in the relaxation frequency of the soft mode arises from the increase in the viscosity of to the system to the collective motion (soft mode); the latter is caused by the unwinding of the TGB helix.

The new process appearing at a frequency of 10 kHz under high bias voltages, seen in figures 7(a) and 7(b), is identified as the deformation process. This appears because the helix is disturbed by the electric field. The reason that it still exists for the helix unwound cell is because the TGB helix cannot possibly be uniformly unwound by the surfaces of the cell. During the procedure of forming a perfect SmA structure by increasing the bias

field, the deformation process will continue to exist. It is interesting to note that a relatively small value of the dielectric loss of this process for the helical unwound cell (see figure 7(b)) compared with that for the helical cell (see figure 7(a)) is found. This is interpreted in terms of less deformation under a bias field for a helix unwound system.

4. Conclusions

Dielectric spectra show a different response for the TGBA* phase from that for the SmA phase. The spectra without bias show a new relaxation process in addition to the soft mode. The spectra with bias exhibit still another new relaxation process. The findings can be summarized as follows.

(i) The dielectric spectra in the absence of the direct bias voltage for the helical TGBA* phase as a function of temperature exhibit two relaxation processes. These are assigned as (a) the soft mode and (b) the molecular relaxation process in the grain boundaries. The dielectric spectra for a thin cell, with the TGB helix having been almost unwound, exhibit only the soft mode, which is similar to that in the SmA phase.

(ii) The dielectric spectra for the SmC*–TGBA* transition suggest a weakly first-order phase transition. This observation supports the conclusion previously made from pitch measurements and DSC.

(iii) The effect of direct bias voltage on the dielectric response of the TGBA* phase is clearly different from that of the SmA phase in two ways. Firstly, the relaxation frequency of the soft mode decreases instead of increasing with increase in the bias voltage. This is because the TGB helix is unwound by the electric field. Secondly, another relaxation process has been found to emerge for higher bias voltages. This is likely to be the deformation process which arises because the TGB helix is disturbed by the electric field. To understand these observations fully, we need to elucidate the important role played by the grain boundaries in the TGBA* phase.

Acknowledgments

The research of the Dubin group was partly funded by the HCM Project CT930353 and by the Programme for Advanced Technology in Materials of the Government of Ireland.

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