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INVESTIGATION OF THE FERRIELECTRIC SUBPHASE WITH q_T>1/2 UNDER BIAS VOLTAGE

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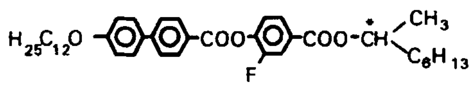
Abstract The properties of Ferrielectric phase with $q_T > 1/2$ have been investigated using broadband dielectric spectroscopy and polarization measurements under the bias voltage. The field -induced sequence of phase transitions is found to be different from those of the conventional ferrielectric phases with $q_T \leq 1/2$.

INTRODUCTION

The competition between ferroelectric and antiferroelectric ordering in adjacent layer produces various ferrielectric subphases between SmC_A and SmC*. According to the Ising model[1], these phases can be characterised by the parameter $q_T = F/(A+F)$ denoting the fraction of ferroelectric ordering (F) which appears in the antiferroelectric structure (A). Although several ferrielectric phases with $q_T \leq 1/2$ were experimentally found[2-3], the existence of the phases with q_T higher that 1/2 have not been reported. In our recent papers[4-5] we reported the appearance of ferrielectric phase with $q_T > 1/2$. This phase is found to be thermodynamically unstable and it co-exists together with the SmC* phase. The application of bias voltage to this phase causes the unusual phase transition which is different from that of the field-induced Devil's Staircase. The structure of these field induced subphases has been investigated using high frequency dielectric spectroscopy and polarization measurements.

EXPERIMENTAL

We provide investigations of the AFLC sample under bias voltage for cells of sample thickness 50 μm to provide the bulk conditions. The AFLC sample used in the experiments was AS-573 (Hull, UK) possessing the following structure and the phase transition sequence (defined by conoscopy and polarization measurements[5]):



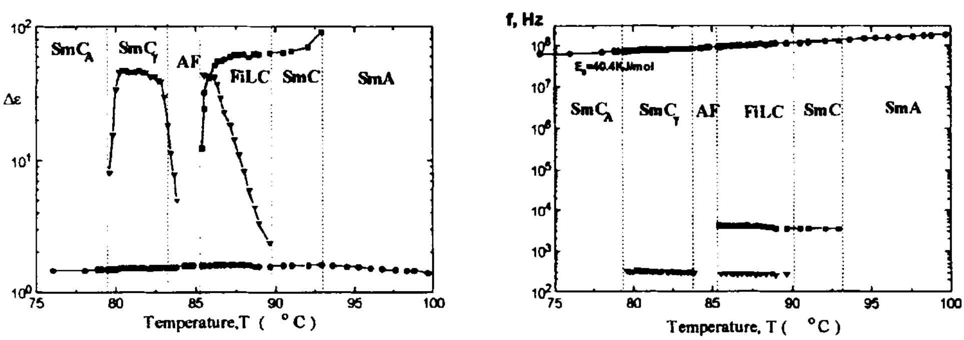
SmC_A 78.3 SmC_γ 83.5 AF 85 FiLC 90 SmC* 93 SmA 105.7 Is

Dielectric measurements were made using Hewlett Packard impedance analysers: HP-4192A (10 Hz - 10 MHz) and HP-4191A (10 MHz - 1 GHz). The spontaneous polarization was measured using the integral reversed current method[6].

RESULTS AND DISCUSSION.

Dielectric spectroscopy

Figure 1 presents the temperature dependence of the dielectric parameters of AS-573. These are found by fitting the dielectric spectra to Havriliak-Negami equation using a fitting programme DK36 developed in Mainz. The relaxation processes in antiferroelectric and SmA phases are omitted in this figure and will be discussed elsewhere. The most interesting region is within a temperature range from 85 to 90°C where two Goldstone processes: ferroelectric (higher frequency) and ferrielectric (lower frequency) are shown to co-exist together.



(a) (b)

FIGURE 1. Dependence of the dielectric strength (a) and relaxation frequency (b) on temperature for AS-573, d=50 μm. •-β- relaxation around long axis, ■- ferroelectric and ▼ - ferrielectric Goldstone modes.

This phenomenon has been explained in terms of a co-existence of two different phases[4]: SmC* and ferrielectric FiLC with q_T parameter higher than 1/2. The highest frequency process just observed in the various phases from SmC_A to Isotropic is the molecular relaxation process around long molecular axis (β- relaxation). The results presented in Figure 1 show that the relaxation frequency of the molecular process obeys the Arrhenius law, however the dielectric strength exhibits a complicated behaviour. In isotropic (not shown in Figure 1) and SmA phases, the dielectric strength increases with a decrease in temperature in agreement with Debye theory and then begins to decrease after passing SmC*-SmA transition. To explain this phenomenon we introduce some geometric factors which affect the dielectric strength of the β- relaxation processes.

Let us assume that the long molecular axis makes an angle ϑ with respect to the plane of the electrodes. The dipole moment μ has a component along the long molecular axis μ_l and a transverse component μ_t such that $\mu = \mu_t + \mu_l$. The application of the electric field will bias the dipolar rotation and induce polarization along (P_l) and perpendicular (P_t) to the long molecular axis. The static susceptibility χ_l of the beta relaxation for rotation around the long axis (β_l), that appears perpendicular to the long molecular axis depends on angle ϑ through the following equation:

$$\chi_l(\vartheta) = \chi_{l0} \cos^2 \vartheta \tag{1}$$

where χ_{lo} is the maximum static susceptibility of the β-relaxation for rotation around the long axis and can be found for planar orientation in the SmA phase.

For a cell in the bookshelf structure the angle ϑ can be found from the following geometric expression:

$$\sin \vartheta = \sin \theta \cdot \sin \varphi, \tag{2}$$

where φ is the azimuthal angle and θ is the smectic tilt angle.

On integrating Equation 1 for small angle $\theta < 1$ over a helical pitch, we find the average susceptibility $\tilde{\chi}_l$ to be

$$\tilde{\chi}_l = \chi_{l0}\left(1 - \frac{\theta^2}{2}\right) \tag{3}$$

Therefore the dielectric strength for the high frequency β-relaxation in the helical phase is smaller than in the unwound SmC* (or SmA) structure by $\theta^2/2$. This is in agreement with the experimental data (Figure 1) where a decrease of the dielectric strength could be explained by the increase of the molecular tilt angle θ in the helical phases.

We thus find that the dielectric strengths of molecular dynamical process is sensitive to the average angle between the molecular director and the surface of the electrodes and this formalism can be used as a basis for the determination of the molecular structure present in the cell under a bias voltage.

Effect of Bias Voltage on the Properties of the Ferrielectric Phase.

The application of the bias voltage to the FiLC phase considerably changes the dielectric spectra (Figure 2).

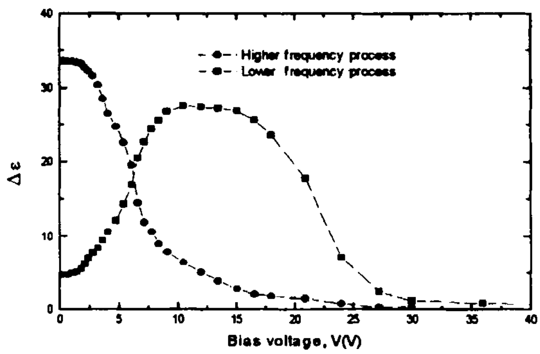
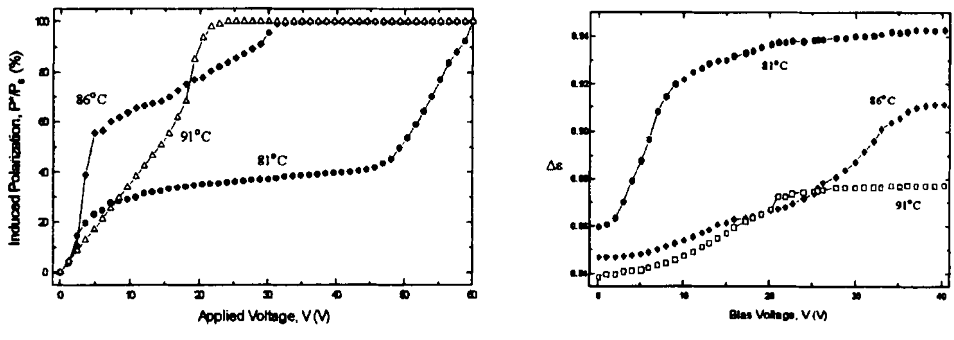


FIGURE 2. Dependence of the dielectric strength on the bias voltage for AS-573, d=50 μm, T=86°C. • - ferrielectric relaxation , ■- ferroelectric relaxation .

At small bias voltage (<2V) we have two dielectric relaxation processes. Then an increase in the bias voltage suppresses the low frequency relaxation mode and causes an amplitude of the high frequency process initially to increase and then to decrease with an increase in the bias voltage. This phenomena could be explained by the coexistence of two phases FiLC and SmC* in this temperature range. An application of the electric field would cause the transition from FiLC to SmC*. This will cause a suppression of the ferrielectric mode in dielectric spectra and an increase in the ferroelectric mode. A further increase of the electric field will unwind the helix and suppress the ferroelectric Goldstone mode.

An application of the bias voltage in this FiLC phase causes the most interesting dependencies of the spontaneous polarization on the applied voltage. Figures 3(a) and 3(b) show the dependence of the normalized macroscopic polarization - $P(V)/P_S$ and dielectric strength of the high frequency β- relaxation as a function of the direct bias voltage for different temperatures (i.e. different phases).



(a) (b)

FIGURE 3. Dependence of the induced polarization (a) and dielectric strength (b) on the bias voltage for AS-573, d=50 μm for different temperature.

In the FiLC phase for voltages in the range 5 V - 30 V, there exists a field induced quasi-stable state with a sufficiently stable and high value of the induced spontaneous polarization. This state was assigned to the field induced Devils' staircase[4]. A comparison of the results on the induced polarization with those of the dielectric strength for the β- relaxation under direct bias voltage (Figure 3(b)) should further clarify the structure of this field induced state and may to lead to a different explanation.

The polarization plot corresponding to SmC_γ phase (81°C) shows a typical ferrielectric dependence of polarization on voltage. For voltages in the range (0V<V<5V) polarization obeys linear dependence on voltage, corresponding to a distortion of the helix, then a saturation value of $P_S/3$ for an unwound ferrielectric structure is reached. Finally at high voltages (> 60 V) the macroscopic polarization reaches a saturation value of P_S. For this phase, the dielectric strength of the β- relaxation reaches a maximal saturation value at 15-20 V (Figure 3b) when the induced polarization becomes $P_S/3$.

For SmC* (T=91°C) and FiLC (T=86°C) phases, the normalised polarization and the dielectric strength together reach a saturation value for the unwound SmC* structure. Therefore a field induced quasi-stable state in the FiLC phase for the voltage in the range 5 V - 30 V is most probably a deformed ferroelectric helical phase. This assignment is supported by the results of several different techniques:

- There exists only one ferroelectric Goldstone process in dielectric spectra in this temperature (T=86°C) and voltage (5 V - 30 V) range as shown in Figure 2.
- The conoscopy pictures for these conditions are typically "ferroelectric-like"[5].

The most probable explanation of these observed effects is to assume the existence of a ferrielectric mesophase with q_T = m/n =3/5 or 5/7. According to Fukuda et al[2] this mesophase with $q_T > 1/2$ could not have the stable existence and could easily be affected by the electric field. Under the bias voltage, the phase transformation cannot be explained by the field -induced Devil's Staircase because of the unusual results of β-relaxation and those of conoscopy both under varying bias voltage. In this case the typical field induced phase sequence FiLC(helical) →FiLC(unwound) → FLC(unwound) could be as FiLC(helical) → FiLC(distorted helical) →FLC(distorted helical)→FLC(unwound). This sequence of transitions explains the results that have been obtained using a number of techniques given above.

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