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Amplitude and phase fluctuation modes of a newly synthesized anti ferroelectric liquid crystal material 4F6Bi

Aanchal Dwivedi [a], R. Dhar [a,b,*], M.B. Pandey [a], I.M.L. Das [a], R. Dabrowski [c]

[a] Physics Department, University of Allahabad, Allahabad-211002, India
[b] Materials Research Laboratory, Physics Department, Ewing Christian College, University of Allahabad, Allahabad-211003, India
[c] Institute of Chemistry, Military University of Technology, Warsaw 00-908, Poland

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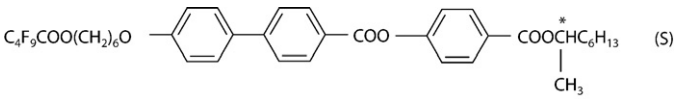
ABSTRACT

Frequency and temperature dependent dielectric spectroscopy of a newly synthesized anti ferroelectric liquid crystal (AFLC) material namely "(S)-(+)-(1-methylheptyloxycarbonyl)phenyl 4′-(6-perfluoropentanoyloxyhex-1-oxy) biphenyl-4-carboxylate ((S) (4F6Bi))" has been carried out in the frequency range 1 Hz to 1 MHz under planar anchoring conditions of the molecules. 4F6Bi possesses paraelectric (SmA^*), ferroelectrics (SmC^*), and wide range anti ferroelectric (SmC_A^*) phases. The SmA^* phase shows soft mode relaxation related with the tilt fluctuations. Its relaxation frequencies are highly temperature dependent and decreases with decrease in the temperature. Dielectric strength is small (~1.0–2.5) but increases with decrease in temperature and follows Curie–Weiss' law. The SmC^* phase shows Goldstone mode with its dielectric strength slowly increasing with decreases in the temperature, and shows maximum value (~64) just above the SmC^*–SmC_A^* transition at 118.1 °C. Goldstone mode relaxation frequency has been found to be almost invariant with temperature (~3.5 kHz). Two modes of dielectric relaxation have been observed in the SmC_A^* phase due to anti ferroelectric ordering of molecules.

1. Introduction

In liquid crystalline systems, the availability of chiral substances of high optical purity has led to the discovery of novel structures like ferroelectric and anti ferroelectric phases [1–3]. Ferroelectric properties in the chiral SmC (SmC^*) phase of liquid crystals has been initially reported by Meyer et. al. in 1975 on the basis of symmetry [4]. In the SmC^* phase, molecules are tilted with respect to the layer normal and direction of tilt (i.e. azimuthal angle) and hence spontaneous polarization (P_S) precesses from layer to layer around an axis (called helix axis) and thus forming a helical structure as shown in Fig. 1. Anti ferroelectric liquid crystals (AFLCs) are also chiral tilted smectics in which the direction of tilt and hence spontaneous polarization in the neighboring layers (called anti tilt pairing layers) point in the opposite directions (see Fig. 1) and thus canceled out. This implies lack of macroscopic spontaneous polarization in the anti ferroelectric (SmC_A^*) phase. AFLCs have excellent properties like tri-state switching, easy DC compensation, microsecond response, gray scale capability, and wide viewing angle. But, the cell made from AFLC materials suffers from the problem of pretransitional effect and leakage of light in dark state due to which devices have poor contrast. These problems could be solved by the improvement in alignment. However, a new class of AFLCs in which directors of molecules in alternating layers are orthogonal to each other and hence named orthoconic AFLCs is expected to solve the problem [5].

Recently, Dabrowski group from Warsaw has been synthesized orthoconic AFLCs with fluorinated terminal chain [6] which show SmC_A^* phase with a broad temperature range near room temperature. Few materials of synthesized series belong to orthoconic de Vries group [7]. Orthoconic de Vries AFLCs are specifically very important from application point of view because of low layer shrinkage at SmA^*–SmC^* transition [8,9]. In the present work, we are reporting the dielectric study of such a orthoconic de Vries material named (S)-(+)-(1-methylheptyloxycarbonyl)phenyl 4′-(6-perfluoropentanoyloxyhex-1-oxy) biphenyl-4-carboxylate (in short 4F6Bi) [7]. The molecular structure of the compound is given below.



This compound possesses paraelectric (SmA^*), ferroelectric (SmC^*) and anti ferroelectric (SmC_A^*) phases with following phase sequence (with transition temperature given in the parentheses in °C) as obtained from Differential Scanning Calorimeter (DSC) measurements in the cooling cycle.

$$\text{Iso}\rightarrow(134.3\ ^\circ\text{C})\text{SmA}^*\rightarrow(124.7\ ^\circ\text{C})\text{SmC}^*\rightarrow(121.4\ ^\circ\text{C})\text{SmC}_A^*\rightarrow(39.7\ ^\circ\text{C})\text{Cr}$$

Here Iso and Cr represent isotropic and crystal phases respectively.

* Corresponding author. Physics Department, University of Allahabad, Allahabad-211002, India. Tel.: +915322413280; fax: +915322466122.
E-mail address: dr_ravindra_dhar@hotmail.com (R. Dhar).

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2. Experimental techniques

The complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) in different mesophases of the planar aligned sample of thickness 10 μm have been measured in the frequency range of 1 Hz to 10 MHz using a Solartron (SI-1260) impendence/gain phase analyzer, coupled with a Solartron dielectric interface (model-1296). The planar alignment was achieved by depositing a thin layer of polyamide nylon on ITO coated glass electrodes of sheet resistance ~25Ω/□, and then unidirectional rubbing is done with soft cotton. The temperature of the sample has been controlled with the help of a hot stage (Instec HS-1) with an accuracy of ±0.1 °C. The temperature near the sample has been measured using a copper-constantan thermocouple with the help of a six and half digit multimeter. The data have been acquired during cooling cycle of the sample from its isotropic phase.

In order to analyze the measured data, real (ε') and imaginary (ε'') parts of the complex dielectric permittivity (ε^*) spectra have been fitted with the generalized Cole–Cole equation [10,11],

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon'(\infty) + \sum_i \frac{(\Delta\varepsilon_i)}{1 + (j\omega\tau_i)^{(1-h_i)}} + \frac{A}{\omega^n} - j\frac{\sigma_i}{\omega\varepsilon_0} - jB\omega^m \quad (1)$$

Here $\Delta\varepsilon_i$ ($\Delta\varepsilon = \varepsilon'(0) - \varepsilon'(\infty)$), τ_i, and h_i are the dielectric strength, relaxation time (inverse of angular relaxation frequency), and symmetric distribution parameter ($0 \le h_i \le 1$) of the ith mode respectively. $\varepsilon'(0)$ and $\varepsilon'(\infty)$ are the low and high frequency limiting values of the relative dielectric permittivity respectively. The third and fourth terms of Eq. (1) represent the contribution from electrode polarization capacitance and ionic conductivity (σ_i), respectively, at low frequencies [12]. A and n are fitting constants [12]. ε_0 (=8.85 pF/m) is the free space permittivity. The fifth term is added in Eq. (1) due to the finite resistance of ITO coated on electrodes above 100 kHz [13–15] where B and m are fitting constants. The characteristic parameters ($\Delta\varepsilon, f_r, h$) of the observed relaxation modes in different phases have been calculated by fitting Eq. (1) with the experimental data. The maximum uncertainty in the measurement of dielectric permittivity (ε') and dielectric loss (ε'') within the entire frequency range is 2%. The uncertainty in the

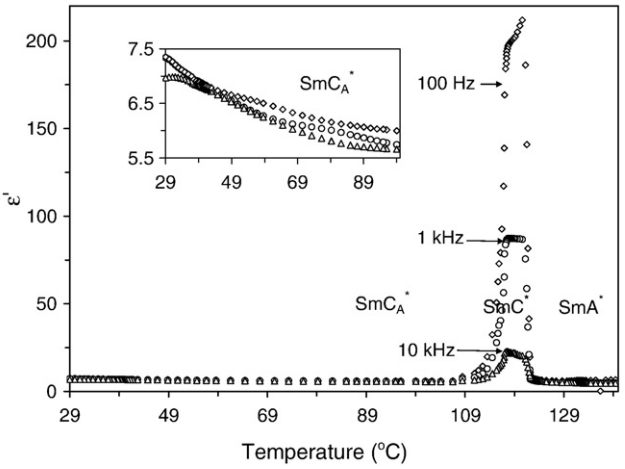

Fig. 2. Temperature dependence of the relative dielectric permittivity (ε') at 100 Hz, 1 kHz and 10 kHz (top to bottom). High value of the permittivity in the ferroelectric SmC* phase clearly distinguishes paraelectric SmA* phase (right) with the anti ferroelectric SmC^*_A phase (left). Inset shows expanded view of the SmC^*_A phase.

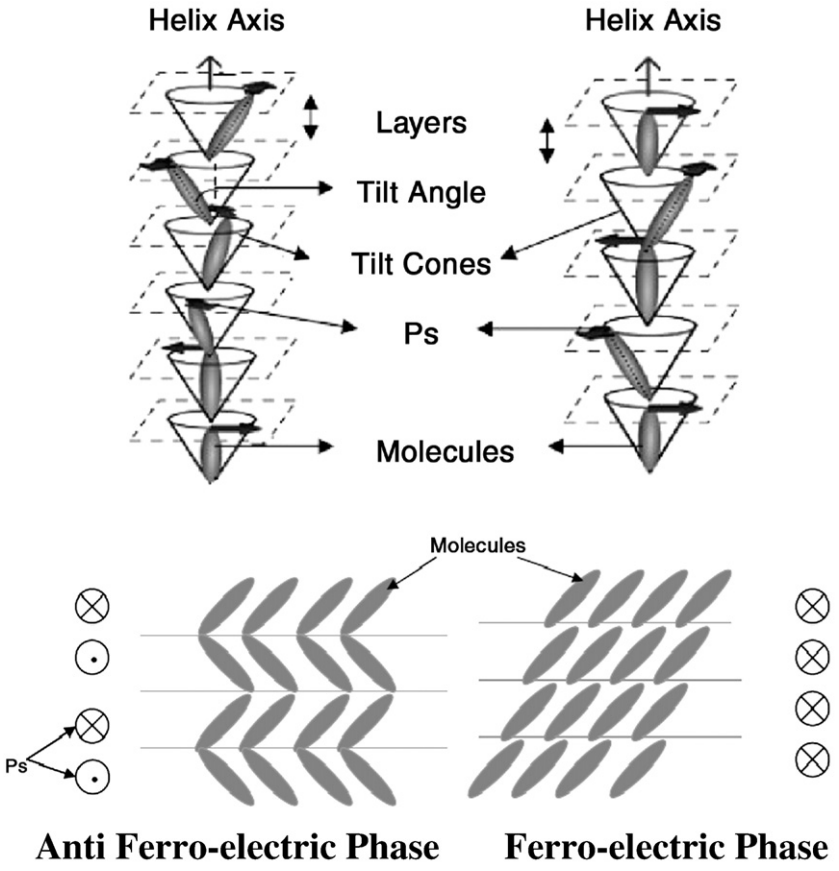

Fig. 1. The helical (upper part) and surface stabilized (lower part) structures of ferroelectric (SmC*) and anti ferroelectric (SmC^*_A) phases.