Thermodynamic and bias field characterization of a quickly operating antiferroelectric liquid crystal

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ABSTRACT

Dielectric relaxation spectroscopy of a quickly operating antiferroelectric liquid crystal (W-204D) has been carried out under the influence of bias electric field in the frequency range of 20 Hz–20 MHz in planar aligned cells. W-204D represents both antiferroelectric (SmC_A^*) and ferroelectric (SmC^*) phases. The temperature dependent dielectric investigation has been studied to explore its effect on the dielectric parameters, where a couple of relaxation modes were observed in SmC^* phase. Dielectric characterization reveals a Goldstone mode around 32.595 kHz and a Soft mode at ~100 kHz in the SmC^* phase. To study the collective relaxation processes between these two modes W-204D was examined under the influence of DC bias electric field. Due to helical unwinding at 30 V bias Goldstone mode get totally suppressed. Experimental data was modeled by Debye and Cole–Cole method indicated that the relaxations are of non-Debye type. Dielectric variations, distribution parameters and relaxation frequencies of these modes have been calculated at various temperatures.

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1. Introduction

Meyer and his coworkers discovered ferroelectricity in liquid crystals in 1975. They reported a large linear electro-optic effect in a new chiral smetic material, and also investigated the effect of DC electric field [1]. The antiferroelectric liquid crystal (AFLC) was initially synthesized by Levelut et al. in 1983 [2] and antiferroelectricity was first recognized by Chandani et al. in 1989 [3]. Since then in the last few years, most valuable results have been drawn from the AFLCs from an application point of view. A very large number of AFLCs materials were then synthesized and characterized by different groups [4,5]. The collective and non-collective molecular dynamics in antiferroelectric SmC_A^*, ferroelectric SmC^* and paraelectric SmA of these liquid crystalline materials have been studied by many authors [6–8]. Due to their interesting physical properties, short switching time and high optical tilt angle in the room temperature range, today's research is getting focused on finding new antiferroelectric liquid crystal (AFLC) materials in high resolution microdisplays [9]. A new type of AFLC having a tilt angle equal to 45°, the so-called orthoconic antiferroelectric liquid crystal (OAFLC), gives a perfect dark state when viewed under crossed polarizers [10–12]. Liquid crystals exhibiting an antiferroelectric phase generally possess the phase sequence Cr–SmC_A^*–SmC^*–SmA–Iso upon heating. Antiferroelectric SmC_A^* phase is also determined by an alternation of the tilt direction of the average molecular orientation. As of its significance, two

smectic layers alternate the trend of in-plane spontaneous polarization $P(r)$ virtually by 180°. These two adjacent layers thus form an antiferroelectric unit cell with two nearly antiparallel (opposite spin) electric dipoles and have a very small value of the effective equilibrium electric polarization $P_o(r) = P_i + P_{i+1} \approx 0$. This in-plane spontaneous polarization spirals with respect to the smectic layer normal (k) in a helical fashion. The helicoidal arrangement of these smectic phases can be distorted by various parameters such as, cell preparation technique; direction of external electric field applied to the helical axis and applied temperature [13–16]. The extinction of the helices highly influences the dielectric properties of the AFLC materials and lead to the formation of novel relaxation modes. These effects can be investigated using the dielectric relaxation spectroscopy (DRS) [16]. In the case of ferroelectric liquid crystal phase (SmC^*), its ferroelectricity is characterized by a layer structure in which the director (n) is tilted by an angle θ with respect to the smectic layer normal (k). SmA phase is a non tilted smectic phase, which can also be identified as a paraelectric phase [17].

DRS enables us to determine the dynamical properties of the system, which are primarily interesting near the phase transitions, where all molecular dynamics of the system can be observed. In the dielectric characterization, SmC_A^* phase permittivity (ε') has in phase collective excitation of the molecules which can be described in two characteristic relaxation modes (AFM1 and AFM2). Whereas AFM1 corresponds to low frequency which can also be described as LFM (low frequency mode) and AFM2 is a high frequency relaxation mode. The bias voltage applied for the characterization of these two modes in the region of SmC_A^* phase is very insufficient. Thus even in

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some reported results, there is no resemblance of applied bias voltage dependence of the dielectric properties of AFM1 and AFM2 [13,18,19]. Furthermore, information on the form of novel relaxation modes and changes in their dielectric characteristics with the applied bias electric field has been inadequate. The orientational phase fluctuation in the limit of small wave vectors and ionic diffusion contributes in showing the Goldstone mode (GM) in SmC* phase. The Goldstone mode can be determined at relaxation frequency which is not found beyond few kHz. Soft mode (SM) is mostly observed in the vicinity of paraelectric and ferroelectric phases which is under the influence of fluctuations in the tilt-angle of the director [20,21].

In the present work, the aim is to explore the outcome of bias electric field on the dielectric properties of different relaxation modes (determined with and without the application of field) of the ferro- and antiferroelectric phases of the AFLC material W-204D. This quickly operating long pitch material (rise time 21 μs, fall time 84 μs) was recently formulated [11] by Dabrowski's group and belongs to very intermediately tilted (Tilt angle ~ 32°) AFLCs [12]. The regular AFLCs have a tilt angle around 20° whereas OAFLCs have a value around 45°. Because of a more tilt angle, OAFLC materials give high optical contrast and this effect is explained elsewhere [10,22]. However, switching time/response time of OAFLC materials is customarily longer as compared to the regular mixture of AFLCs [11]. Material W-204D combines the advantages of AFLC and OAFLC and is quickly operating as compared to the other materials investigated [12] The material investigated in the present work has an intermediate tilt angle. The Cole–Cole plot has been used to find out the dependence of distribution parameter (α), dielectric strength ($\Delta\hat{\epsilon}$) and relaxation frequency (f_c) as a function of temperature. In addition to dielectric studies, thermal analysis of this AFLC material has also been described to recognize the phase transition temperatures.

2. Experimental

R. Dabrowski group at the Military University of Technology, in Warsav, Poland, has formulated W-204D, it exhibits an antiferroelectric phase at around room temperature. It also represents ferroelectric and smectic A phases at a wide temperature range. The phase progression of this material is as follows: Cr − 5 °C–SmC$_A$* − 71 °C–SmC* − 90 °C–SmA − 105.4 °C–Iso determined from DSC measurements. The characterization and electro-optical study of W-204D are given elsewhere [11,12] and the temperature dependence of pitch is given in Fig. 1.

2.1. Construction of the cell

Indium tin oxide (ITO) coated glass substrates were spin coated with polyimide at 3000 rpm and they were dried at 60 °C for ~1 h. The thickness of the coating was ~50 nm and these coating layers were exposed to the surface treatment of unidirectional rubbing
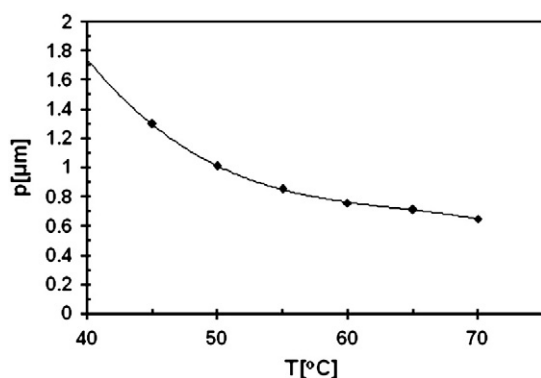

Fig. 1. Temperature of selective reflection p calculated.

with a velvet cloth in order to obtain planar molecular alignment. The debris formed on the surface because of rubbing process was removed by blowing with N$_2$ gas. An empty cell assembly was fabricated by putting a poly(ethylene terephthalate) (PET) film spacer of suitable thickness between the two ITO-coated glass plates, facing their conducting sides each other. The entire assembly was then sealed by applying UV-curable adhesive along the two opposite edges. Then AFLC cell was filled by a capillary method in the isotropic phase.

PT 100 resistor was in direct contact with the sample to control the temperature of the sample. Temperature was monitored between 30 °C and 110 °C with an accuracy of ± 0.1 °C by using Electrotech Temperature Control system. The area and surface resistance of the ITO coated glass electrode were 3.68 cm^2 and 5.59 Ωcm respectively.

2.2. Thermal analysis

The phase transition from crystal to isotropic state of AFLC W-204D was measured by using a Differential Scanning Calorimeter (DSC) (TA Instruments, Waters, India). The scanning rate of DSC was 5 °C/min, in nitrogen atmosphere.

2.3. Dielectric relaxation spectroscopy

Study of dielectric properties of the planar aligned sample of thickness 6 μm has been carried out in the frequency range of 20Hz–20MHz with the maximum applied voltage of 0.5 V (RMS) by using a Precision Impedance Analyzer (Wayne Kerr 6500B, 0-40 DCV, UK). The error in the measurement of capacitance (C) and Dissipation factor (tan^{-1})$_⊥$ in the applied frequency range was <1% and the graphs were plotted using the average of three sets of readings. The relative dielectric constant was obtained for the measurement from the parallel capacitance using the following formula [23,24].

$$\epsilon_r = \frac{C_p}{C_0} = \frac{C_p \times D}{A \times \epsilon_0} = \epsilon'_⊥ \qquad (1)$$

where ($\epsilon_r/\epsilon'_⊥$) is relative dielectric constant/permittivity, (C$_p$) is parallel capacitance, (D) is the thickness of composite film, (A) is the area of electrode and (ϵ_0) is free space permittivity and its value is 8.854×10^{-12} F/m.

3. Results and discussion

3.1. Experimental characterization

The thermal analysis was carried using DSC. 3.63 mg of sample W-204D was taken for the study. The heating/cooling rate was maintained at 10 °C/min between 40 °C and 120 °C. DSC curves taken for W-204D are presented in Fig. 2. As one can see, the sequence connected with the transitions Cr–SmC$_A$*, SmC$_A$*–SmC*, SmC*–SmA, SmA–Iso is well noticeable.

The existence of three phases, wiz SmC$_A$*, SmC* and SmA, is clearly visible in Fig. 3, where the maxima of $\epsilon'_⊥$ in ferroelectric SmC* phase is observed and it separates the paraelectric SmA and antiferroelectric SmC$_A$* phases. The temperature dependence of the dielectric permittivity ($\epsilon'_⊥$) is more or less constant in the SmA phase measured for 1 MHz and 20 MHz frequencies (see Fig. 3). During the SmC$_A$* phase, the dielectric permittivity ($\epsilon'_⊥$) is almost constant for all the frequencies measured. However, when the temperature is increased to 70 °C, there is a transformation of phase from SmC$_A$* to SmC* phase, and results in an increase of $\epsilon'_⊥$. The increase in $\epsilon'_⊥$ is more prominent for frequencies 100 kHz and 1 kHz. At the end the Soft SmC* mode (uniform tilt of molecules) contributes to the decrease of the dielectric constant. Thereafter (in SmA phase), the values $\epsilon'_⊥$ decrease with an increase in frequency, due to the contribution of electrode polarization capacitance and ionic conductance at all temperatures [25,26].