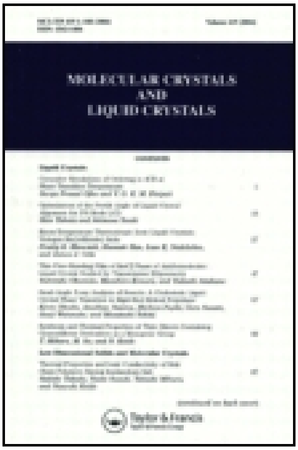

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Dielectric Properties of New Fluorinated Orthoconic Antiferroelectric Liquid Crystals

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Three different Antiferroelectric Liquid Crystals, synthesized in Military University of Technology were investigated by dielectric means. Some of them are orthoconic. The structures of studied compounds are very similar. The only one difference is presented in rigid core. The position and number of Fluorine atoms in rigid core changes. Very rich dielectric modes are detected with frequencies from 50 Hz up to 40 MHz. In this paper, dielectric spectroscopy of investigated materials is presented.

Keywords: dielectric modes; dielectric spectroscopy; smectic liquid crystals

INTRODUCTION

Dielectric spectroscopy is a very powerful experimental technique in liquid crystal investigation [1–3]. Because of reach polymorphism of smectic liquid crystals, this method is useful for identyfication smectic sub-phases [1,3,4].

Three single, Antiferroelectric Liquid Crystals (AFLC) (some of them are orthoconic – with tilt angle around 45°), presented in the Figure 1, were synthesized in Military University of Technology [5].

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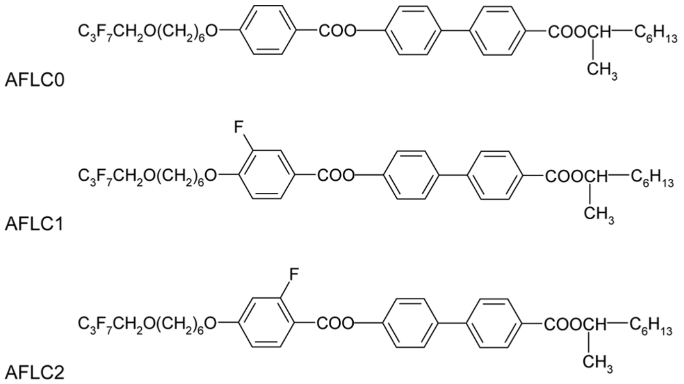

FIGURE 1 Molecular structure of investigated materials.

They have quite similar structures. The only difference within the molecular structure is the number and position of Fluorine atoms in molecular rigid core.

EXPERIMENT

Experiments were performed using custom made cells. The conductive layers were done by evaporating a thin layer of gold. The proper resistivity of golden layers were approximate around a $1\Omega/\square$. Connection between wires and cell electrodes was made with ultrasonic welding unit ULTRASONIC-400 (Industrial Technologies AB). LC sample, with 9 μm gap and planar alignment, was slowly cooled from isotropic phase at 0.1°C/min rate. For this purpose Linkam TMHSE 600 hot stage with Linkam TMS 93 temperature controller, were used. Dielectric measurements were prepared by HP 4192A (Hewlett Packard impedance analyzer) at frequencies from 100 Hz up to 10 MHz with weak AC measuring field (0.1 V) to avoid nonlinear response. A few BIAS voltages (0 V, 5 V, 9 V, 15 V, 20 V, 28 V) were used, to suppress Goldstone mode, as well as to investigate the BIAS influence on dielectric modes in AFLC.

RESULTS OF MEASUREMENTS

In the Figures 2–4, relaxation frequencies for all modes detected in smectic phases for all investigated materials, are presented. Frequencies are calculated according to the Cole – Cole dielectric relaxation model.

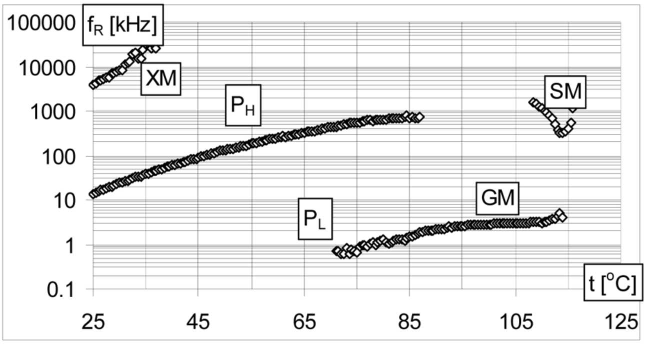

FIGURE 2 Relaxation frequencies (f_R) for AFLC0 in all smectic phases (no BIAS voltage). XM – high frequency mode, P_H – anti-phase mode, P_L – in-phase mode, GM – Goldstone mode, SM – soft mode.

Several dielectric modes are detected in AFLC0: high frequency mode (X-Mode) [6] with relaxation frequency between 3.5 MHz and 30 MHz in antiferroelectric phase; anti-phase antiferroelectric mode (P_H) with frequencies between 10 kHz and 900 kHz (slowly increasing with temperature); in-phase antiferroelectric mode (P_L) with frequencies around 1 kHz (slowly increasing with temperature); Goldstone mode (GM) in ferroelectric phase with constant frequency around 2–3 kHz; and soft mode (SM) with frequencies decreasing from 2 MHz to 300 kHz in SmC* phase and increasing from 300 kHz up to 1 MHz in SmA* phase.

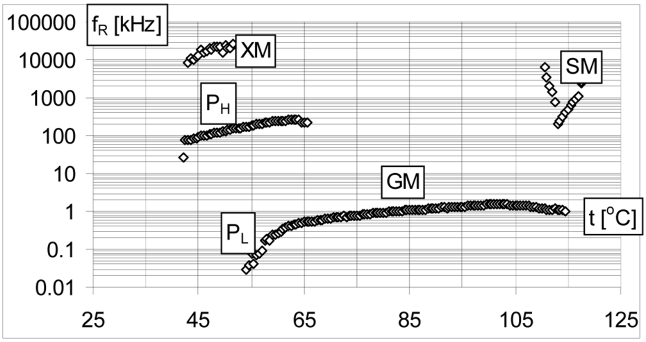

FIGURE 3 Relaxation frequencies (f_R) for AFLC1 in all smectic phases (no BIAS voltage). XM – high frequency mode, P_H – anti-phase mode, P_L – in-phase mode, GM – Goldstone mode, SM – soft mode.

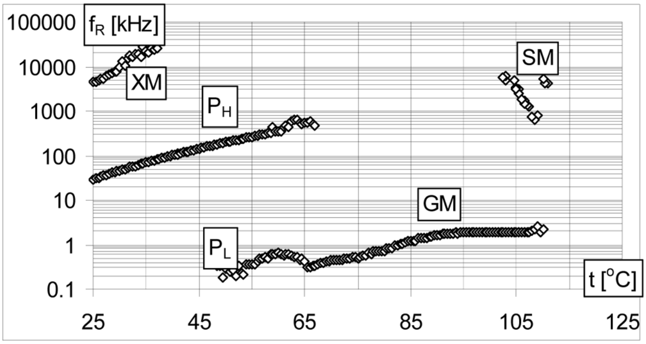

FIGURE 4 Relaxation frequencies (f_R) for AFLC2 in all smectic phases (no BIAS voltage). XM – high frequency mode, P_H – anti-phase mode, P_L – in-phase mode, GM – Goldstone mode, SM – soft mode.

The same modes are detected in AFLC1 and AFLC2. Goldstone modes in AFLC1 and AFLC2 are slower than in AFLC0. Antiferroelectric phase in AFLC0 exhibits 60°C broad temperature range, in AFLC1 around 20°C and in AFLC1 around 40°C.

In Figures 5–7 dielectric strengths are presented for all investigated materials. Generally speaking dielectric strength of X-mode is higher than for P_H. Dielectric strength of P_L is higher than for P_H. Dielectric strength of soft mode has maximum at the temperature of SmC* – SmA* phase transition exactly. The Goldstone mode dielectric strength magnitude for AFLC0 is 4–5 times lower than for AFLC1 and AFLC2. It is worth to underline that dielectric strength of P_H and P_L modes in AFLC0 are lower than for AFLC1 and AFLC2.

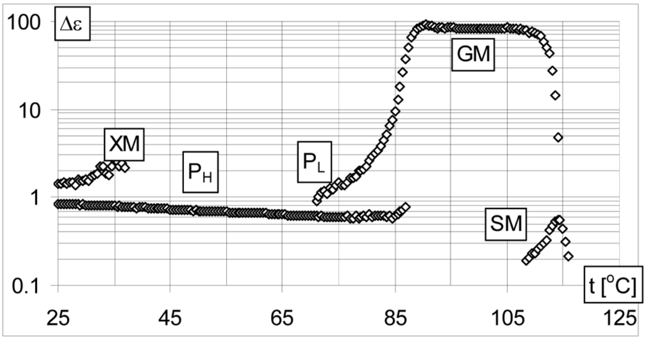

FIGURE 5 Dielectric strength ($\Delta\varepsilon = \varepsilon_S - \varepsilon_\infty$) for AFLC0, for all modes, in all smectic phases.

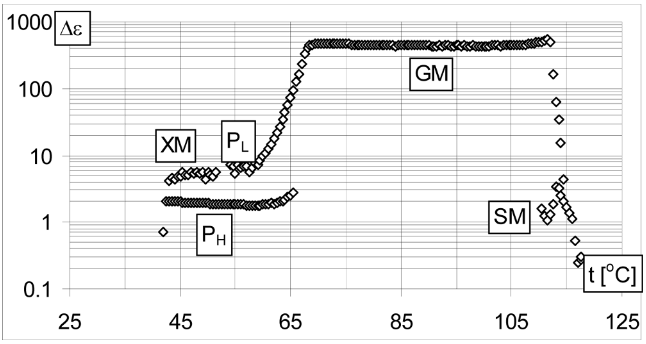

FIGURE 6 Dielectric strength ($\Delta\varepsilon = \varepsilon_S - \varepsilon_\infty$) for AFLC1, for all modes, in all smectic phases.

Because the dielectric behavior of all substances is similar we decided to show dielectric properties for AFLC0, more detailed.

In the Figure 8, ε'' as a function of ε' is presented in SmC_A^* (28°C). One can notice that amplitude of P_H mode is slowly increasing with BIAS field, while amplitude of X-mode is slowly decreasing.

In the Figure 9, ε'' as a function of ε' is presented for SmC_A^* (81°C). It is easy to notice that with BIAS field amplitude of P_L mode (dielectric strength) rapidly decreasing while magnitude of P_H mode is rather constant. But for BIAS field 28 V/9 μm, magnitudes of both modes are rather low. It seems, that for such BIAS voltage, antiferroelectric phase is completely unwound and such structure does not create any dielectric answer [9].

In the Figure 10, ε'' as a function of ε' is presented for SmC^* (112.5°C) – very close to the SmC^* – SmA^* phase transition. Goldstone

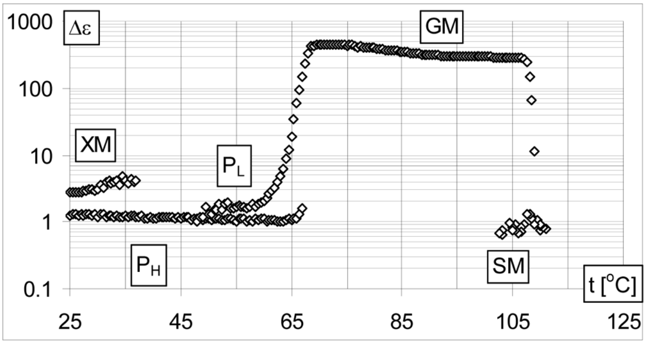

FIGURE 7 Dielectric strength ($\Delta\varepsilon = \varepsilon_S - \varepsilon_\infty$) for AFLC2, for all modes, in all smectic phases.

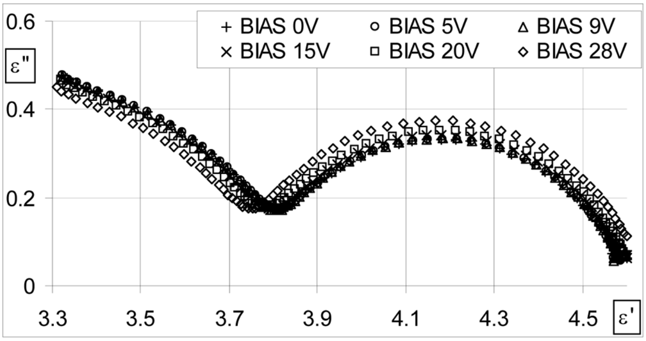

FIGURE 8 Cole – Cole plots (ε'' as a function of ε') for AFLC0 in 28°C for different BIAS voltages.

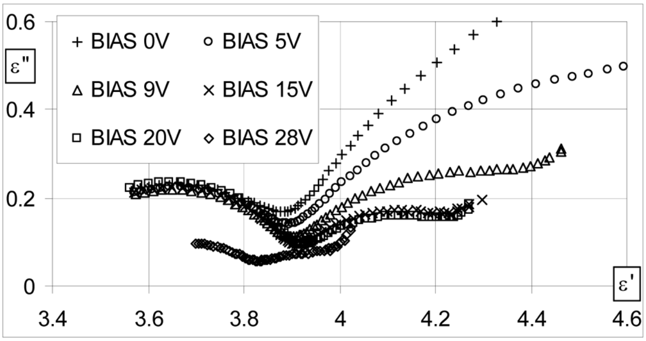

FIGURE 9 Cole – Cole plots (ε'' as a function of ε') for AFLC0 in 81°C for different BIAS voltages.

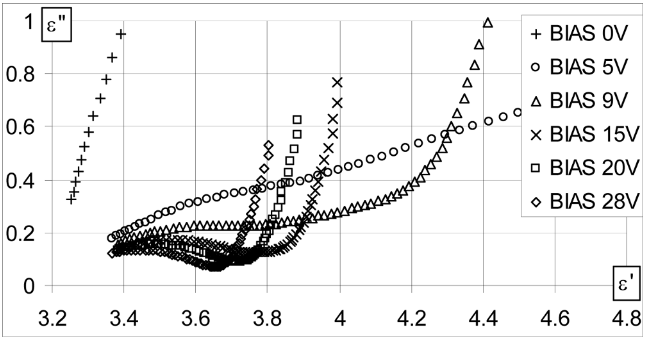

FIGURE 10 Cole – Cole plots (ε'' as a function of ε') for AFLC0 in 112.5°C for different BIAS voltages.

mode rapidly decreasing with BIAS voltage, while soft mode is constant. In fact BIAS field is necessary to suppress Goldstone mode to detect soft mode.

DISCUSSION

We found that the value of dielectric permittivity as well as relaxation frequencies, presented in smectic phases, change from substance to substance. The main reason should be the Fluorine atoms. When the Fluorine atoms are built-in, perpendicular dipole moment increases. Additionally Fluorine atom can more hinder (usually almost free) the rotation around long molecular axis [7,8]. What is interesting Fluorine atoms do not change the phase sequences but influence the phase temperature ranges.

It is still open question (asked in [6]) "what is this X-mode relaxation?". Earlier it was difficult to detect such relaxation because measuring range of cells with ITO electrodes was below 300 kHz. For cells with golden electrodes, it is possible to measure relaxation frequencies up to 10 MHz. The important evidence showing that this mode is not related to internal cell relaxation [2] is fact that high frequency dielectric permittivity (ε_∞) calculated from Cole – Cole plot changes from 2.5 for 25°C to 1.5 for 37°C for X-mode. If it was a cell relaxation, ε_∞ would be less than 1 [2].

This mode (XM) depends on BIAS field very weakly, what one can see in the Figure 8.

For all substances this mode appears close to phase transition SmC_A^* – molecular crystal, and disappears when P_L mode appears. What is interesting P_H mode, detectable for whole SmC_A^* phase coexists with either X-mode or P_L mode (separately).

Is the X-mode a molecular mode? When we compare the magnitude (dielectric strength) of X-mode and P_H mode (which is the collective mode) we can conclude that X-mode should be a collective one. If it was a molecular mode, the magnitude of X-mode should be lower than magnitude of P_H mode.

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