MAREK WOJCIECHOWSKI

Centre of Mathematics and Physics, Technical University of Lodz
Politechniki 11, 90-924 Łódź, Poland
Institute of Physics, Technical University of Lodz
Wólczańska 219/223, 90-924 Łódź, Poland

DIELECTRIC RELAXATION MODES IN ANTIFERROELECTRIC LIQUID CRYSTAL MIXTURE

Mixture of liquid crystals, with induced antiferroelectric phase has been studied by means of dielectric spectroscopy. The dielectric measurements were carried out in a cell with gold electrodes at planar orientation. The characteristic of dielectric relaxation modes in all phases existing in the mixture are presented. The results are compared with the results obtained for the same mixture in the cell with ITO electrodes.

Keywords: antiferroelectric LC, dielectric relaxations, soft mode.

1. INTRODUCTION

After the discovery of antiferroelectricity in liquid crystals, a lot of new compounds showing this effect have been synthesized and investigated. Among many LC antiferroelectric substances, probably the most interesting are those materials which exhibit antiferroelectric phase the room temperature, because of their possible practical application. Antiferroelectric liquid crystals show not only antiferroelectric and ferroelectric phases, but frequently also the smectic chiral subphases (SmC_α, SmC^*_β, SmC^*_γ) [1]. This suggests that chiral smectic C* subphases can occur in new synthesizes antiferroelectric liquid crystal materials and their mixtures. Due to the reasons mentioned above numerous dielectric investigations of new materials are carried out to search anomalies of their characteristics.

In this work the dielectric characteristics of recently synthesizes antiferroelectric liquid crystals mixture, studied in the cell with the gold

electrodes, are presented, analysed and compared with the results earlier obtained in the cell with ITO electrodes [2]. In this work the temperature and frequency dependence of dielectric properties of recently synthesized antiferroelectric mixture has been investigated in the cell with gold electrodes.

2. EXPERIMENTAL

The bicomponent mixture (1:1) of liquid crystalline compounds presented below (which do not exhibit antiferroelectric phase separately) was investigated.

$CNCH_2COO(CH_2)_6O$ - ⬡⬡ -COO ⬡ -COOC*$(CH_2)C_6H_{13}$ (CNH6Bi)

$CH_3COO(CH_2)_3O$ - ⬡ -COO - ⬡⬡ -COOC*$(CH_2)C_6H_{13}$ (1H3B)
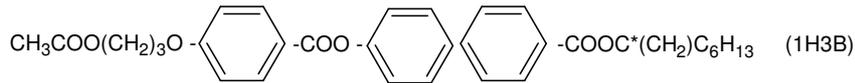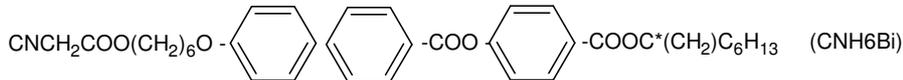
The investigated compounds were synthesized and the mixture was prepared in the Institute of Chemistry, Military University of Technology (Warsaw) [3]. The phase sequence for the two compounds are as follows: Cr→SmA*→Iso for CNH6Bi and :Cr→SmC*→SmA*→Iso for 1H3B [3]. This mixture shows antiferroelectric phase in a broad temperature range near room temperature. The mixture also shows selective light reflection in the blue range at room temperature. The phases sequence in the investigated mixture is as follows [3]:

$$Cr \rightarrow Sm\,C_A^* \rightarrow 38 \div 41^0C \rightarrow Sm\,C_x^* \rightarrow 66 \div 67.5^0C \rightarrow SmA^* \rightarrow 103^0C \rightarrow Is.$$
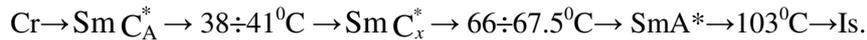
The dielectric measurements were performed for the liquid crystal mixture placed between two parallel glass plates with 5x5 mm gold electrodes. We used standard cells, commercially available from AWAT. The cells used give planar orientation. The sample thickness was d = 5 μm. The measuring sinusoidal signal (0.1V) was applied nearly perpendicularly to the director of smectic layers. The measurements were carried out with Solartron 1260A Impedance Analyser with Chelsea Dielectric Interface in the frequency range 10^{-3} Hz $\div$ $5 \cdot 10^5$ Hz.

The Havriliak-Negami equation was used for fitting the experimental results in the following version:

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = -i\left(\frac{\sigma_0}{\varepsilon_0\omega}\right)^n + \sum_{k=1}^{m}\left\{\frac{\Delta\varepsilon_k}{\left[1+(i\omega\tau_k)^{\alpha_k}\right]^{\beta_k}} + \varepsilon_{\infty k}\right\}$$

where: σ_0 – dc conductivity, $\Delta\varepsilon$ – dielectric strength, τ – relaxation time, α – width parameter, β – asymmetry parameter, ε_∞ – infinite permittivity.

All presented results were obtained in cooling process. The relaxation processes registered in the low frequency region (at about 10 Hz) are related to Maxwell-Wagner relaxation [4] and are not presented because this is a typical cell relaxation process.

3. RESULTS AND DISCUSION

Various dielectric characteristics of the investigated mixture are presented below. Real part of dielectric constant is shown in Fig. 1 for three various frequencies 1 kHz, 10 kHz, 100 kHz, and reflects phase sequence. It is seen that in the temperatures near phase transition SmC*$_x$-SmA*, the dielectric constant changes dramatically, which suggests that the strong relaxation process in this temperature range occurs (soft mode in this case).
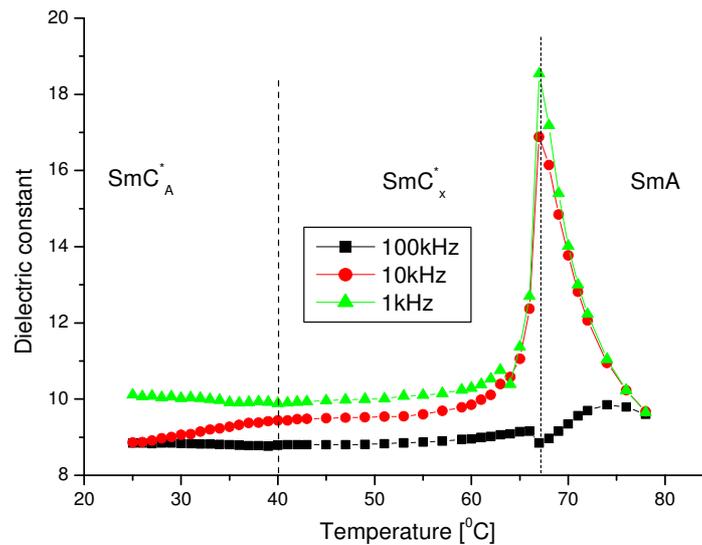
Fig. 1. Real part of dielectric permittivity vs. temperature for various frequencies

Analyzing this temperature dependence and taking into account the temperature dependence of other dielectric parameters presented in the next part of the article, it is possible to propose the following phase transition in the investigated mixture in the cooling process:

$$SmA^* \xrightarrow{67^0C} Sm\,C_x^* \xrightarrow{40^0C} Sm\,C_A^*$$

which is similar to the results obtained using ITO coated cells [2].

During cooling liquid crystalline sample from isotropic liquid to the SmA* phase, the first detected relaxation process occurs in the vicinity to the phase transition to the new phase in the lower temperatures and it is the soft mode. Fitting experimental results to Havriiak-Negami equation gives dielectric strength and relaxation frequencies of the soft mode. The obtained results are presented in Fig. 2 from both sides of SmA*-SmC*$_x$ phase transition.
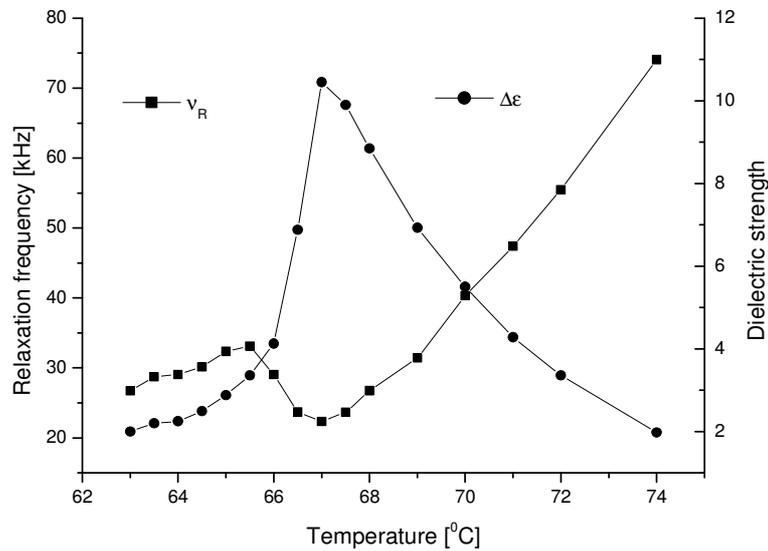
Fig. 2. Soft mode parameters near phase transition SmA*-SmC*$_x$ phase

The first relaxation peak detected in the SmA* phase at 74^0C have relaxation frequency about 75 kHz with the low dielectric strength. The relaxation frequency decreases to about 20 kHz and dielectric strength grows to about 10 in the phase transition, temperature of which could be detected at 67^0C. At another side of phase transition (in the SmC*$_x$) with decrease temperature the relaxation frequency grows and dielectric strength decreases. This is typical temperature dependence of soft mode [5]. The reciprocal of dielectric strength of soft mode near the phase transition is presented in Fig. 3 and confirms Curie-Weiss law.

In the SmC*$_x$ subphase two relaxation processes were detected. The fitting procedure is presented below in Fig. 4.
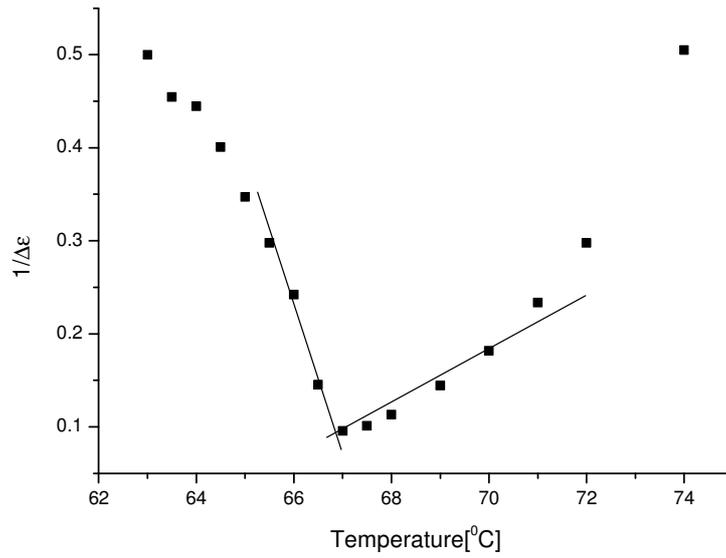
Fig. 3. Reciprocal of dielectric strength of soft mode
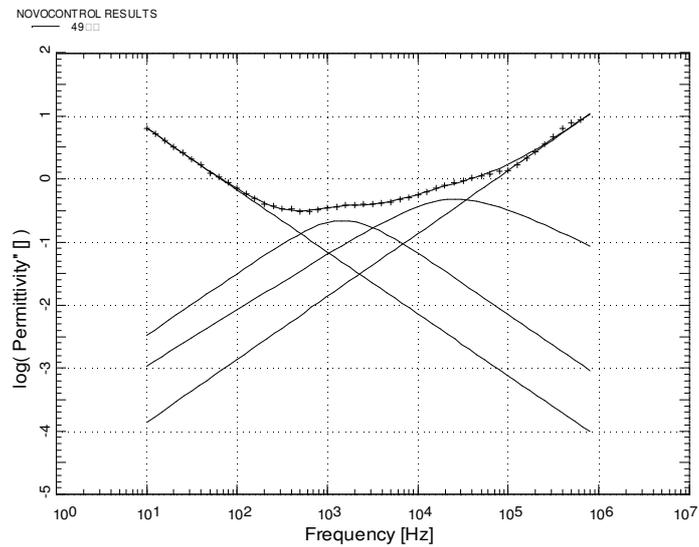
Fig. 4. Fitting procedure to Havrilik-Negami eguation for peaks observed in the SmC*$_x$ subphase

The obtained relaxation frequencies and dielectric strengths for different temperatures for both relaxation processes are presented in Fig. 5 and Fig. 6, respectively.
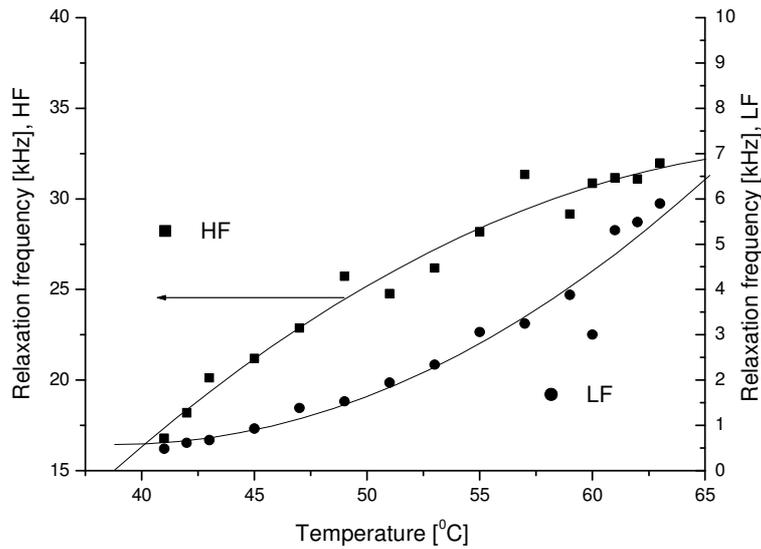
Fig. 5. Temperature dependence of relaxation frequencies for both relaxation processes detected in the $SmC*_x$ subphase

The relaxation frequency of the high frequency process (HF) changes from 18 kHz at 41^0C to about 30 kHz in the vicinity to the phase transition to the SmA* phase. The dielectric strength is about 1 and grows with growing temperature. The relaxation frequency of low frequency process (LF) changes with temperature from about 1 kHz near $SmC*_A$ phase up to 6 kHz near the SmA* phase. The dielectric strength of LF process is less than 1 and decreases with increasing temperature down to about 0.5. Arrhenius plots were made for both relaxation processes. The obtained activation energy for LF was equal to 0.96 eV and for HF equal to 0.24 eV. The interpretation of those modes is rather speculative and LF could be related to the rotation around short axis, but the nature of HF process could be connected with phase inhomogenity of $SmC*_x$ subphase of the investigated mixture. In the case of the cell with ITO electrodes no relaxation peaks in this phase were observed, which suggests that the $SmC*_x$ subphase could be interpreted as a $SmC*_\beta$ subphase.
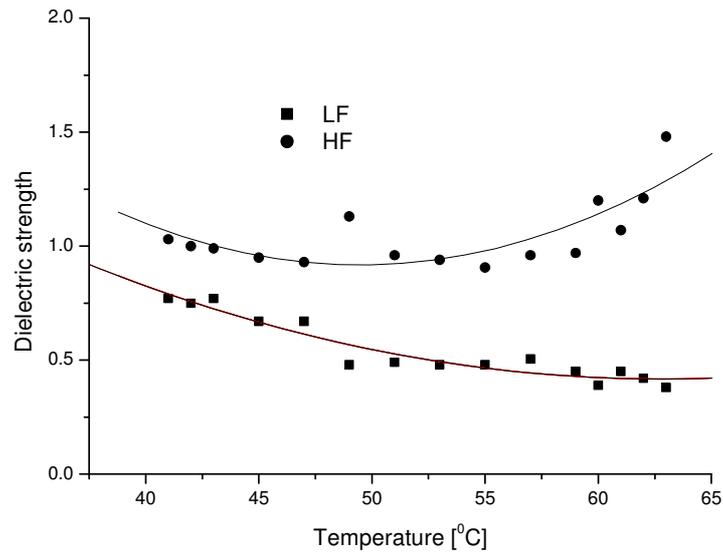
Fig. 6. Temperature dependence of dielectric strength of LF and HF processes
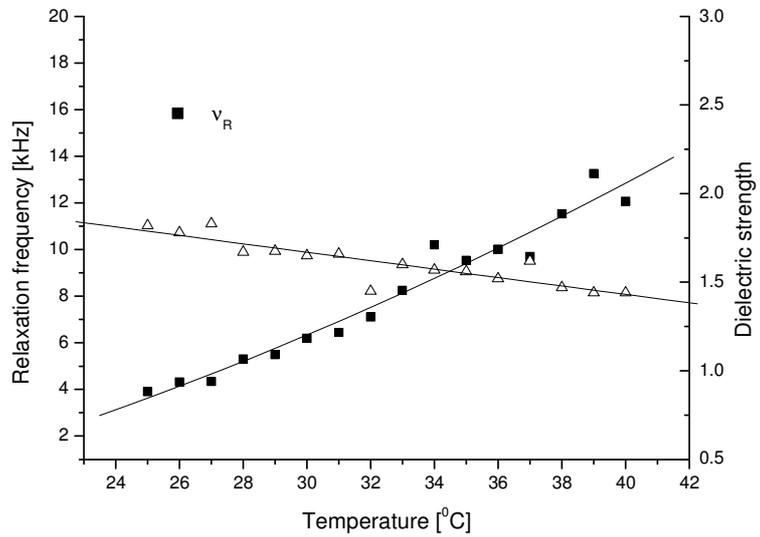
Fig. 7. Temperature dependence of relaxation frequencies and dielectric strength
of relaxation process detected in the SmC*$_A$ phase

In the light of the present results the SmC*$_x$ phase has to be interpreted as an unknown kind of smectic chiral subphase.

In the SmC*$_A$ phase one relaxation mode was detected. The temperature dependence of parameters of this mode is presented in Fig. 7. The relaxation frequency changes slowly with temperature within this phase in the range 4÷13 kHz. The temperature dependence of the dielectric strength is linear and $\Delta\varepsilon$ changes in the range 1.4÷2. The same relaxation process was detected in the cell with ITO electrodes [2], with similar dielectric strength, but with higher relaxation frequencies. This relaxation process is probably one of the collective modes existing in an antiferroelectic phase, so called low frequency P$_L$ mode. The P$_L$ relaxation mode is considered to be related to in-phase azimuthal angle fluctuation of the directors in the anti-tilted molecular pairs [6,7].

4. CONCLUSIONS

1. The temperature dependence of dielectric constant and dielectric characteristics of the investigated mixture in cell with gold electrodes confirms the phase transition diagram obtained in the cell with ITO electrodes [2].
2. The soft mode parameters obtained in two types of cells are similar and temperature dependences are the same.
3. In the SmC*$_x$ subphase in the case of gold electrodes the observed dielectric spectrum shows two relaxation modes, contrary to dielectric spectrum in the ITO electrodes where no dielectric modes were observed. The SmC*$_x$ subphase is a kind of smectic chiral subphase.
4. In the antiferroelectric SmC*$_A$ phase for both types of cells the observed relaxation process is the low frequency mode P$_L$ and is related to the collective excitation of the molecules (in-phase azimuthal angle fluctuation).

REFERENCES

[1]   **Lagerwall J.P.F., Rudquist P., Lagerwall S.T., Gieβelmann F.:** Liq. Cryst., **30** (2003) 399.
[2]   **Wojciechowski M., Bąk G.W., Tykarska M.:** Opto-electronic Rev. **16** (2008) 1.
[3]   **Skrzypek K., Tykarska M.:** Ferroelectrics, **343** (2006) 177.
[4]   **Wojciechowski M., Gromiec L.A., Bąk G.W.:** J. Mol. Liquids, **124**, (2006) 7.
[5]   **Kundu S., Ray T., Roy S.K., Dąbrowski R.:** Liq. Cryst., **31** (2004) 119.

[6] **Buivydas M., Gouda F., Lagerwall S.T., Stebler B.:** Liq. Cryst., **18** (1995) 879.

[7] **Pandy M.B., Dhar R., Agrawal V.K., Dąbrowski R., Tykarska M.:** Liq. Cyst. 31 (2006) 973.

PROCESY RELAKSACJI DIELEKTRYCZNYCH W ANTYFERROELEKTRYCZNEJ MIESZANINIE CIEKŁOKRYSTALICZNEJ

Streszczenie

Spektroskopia dielektryczna została użyta do badań ciekłokrystalicznej mieszaniny z indukowaną fazą antyferroelektryczną (związki ciekłokrystaliczne, z których sporządzono mieszaninę nie posiadają samodzielnie fazy antyferroelektrycznej). W pracy przedstawiono dielektryczne charakterystyki poszczególnych faz oraz interpretację zarejestrowanych procesów relaksacyjnych otrzymanych w komórce o złotych elektrodach. Otrzymane wyniki porównano z wynikami otrzymanymi wcześniej w komórce z elektrodami ITO. Zdecydowane różnice w widmie dielektrycznym zaobserwowano w subfazie SmC*$_x$ co oznacza, że interpretacja tej subfazy jest jeszcze sprawą otwartą.