SCIENTIFIC BULLETIN OF THE TECHNICAL UNIVERSITY OF LODZ
No. 1030 Physics, Vol. 29 2008

MAREK WOJCIECHOWSKI[1,2]

[1]Center of Mathematics and Physics, Technical University of Łodz
Al. Politechniki 11, 90-924 Łódź, Poland
[2]Institute of Physics, Technical University of Łodz
Wólczańska 219/223, 90-924 Łódź, Poland

DIELECTRIC CHARACTERISTICS OF ANTIFERROELECTRIC LIQUID CRYSTALLINE 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.

Keywords: antiferroelectric LC, dielectric relaxations, Goldstone mode.

1. INTODUCTION

Antiferroelectric liguid crystals show a lot of chiral smectic C* phases (ferroelectric SmC* and antiferroelectric SmC^*_A) and subphases (SmC_α, SmC^*_β, SmC^*_γ) with different combinations [1] and additionally at lower temperatures some kind of highly ordered smectic phases can occur [2,3]. The situations is especially interesting and complicated in mixtures in which some chiral smectic C* phases can occur, though they do not exist in pure compounds. Due to the above reasons mentioned numerous dielectric investigations of new liquid crystalline mixtures are carried out to search anomalies of their characteristics.

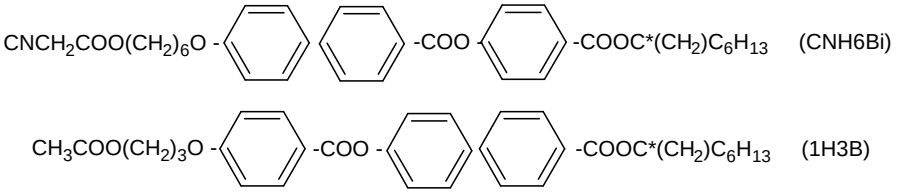
In this work the dielectric characteristics of recently synthesizes antiferroelectric liquid crystalline mixture, studied in the cell with the gold electrodes, are presented and discussed. In the investigated mixture the ferroelectric phase exists.

In our earlier works [4,5] we investigated the mixture of the same compounds, but in another composition (1:1), in which antiferroelectric phase

occurs in a broad temperature range near the room temperature and the ferroelectric phase does not appear.

2. EXPERIMENTAL

The bicomponent mixture (1:9) (mole fractions) of liquid crystalline compounds presented below (which do not exhibit antiferroelectric phase separately) was investigated.



The investigated compounds were synthesized and the mixture was prepared in the Institute of Chemistry, Military University of Technology (Warsaw) [6].
The phases sequence in the investigated mixture is as follows [6]:

$$\mathrm{Cr}\rightarrow 57\text{-}58^{O}\mathrm{C}\rightarrow \mathrm{Sm}\,C_{A}^{*}\rightarrow 77.8\text{-}78.5^{O}\mathrm{C}\rightarrow 88\text{-}88.6^{O}\mathrm{C}\rightarrow \mathrm{SmA}^{*}\rightarrow 99.7\text{-}101^{O}\mathrm{C}\rightarrow \mathrm{Is}.$$

The dielectric measurements were performed for the liquid crystal mixture placed between two parallel glass plates with 5x5mm gold electrodes. We used standard cells, commercially available from AWAT. The cells used give planar orientation. The sample thickness was d = 5μm. 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÷$5\cdot10^{5}$ Hz.

For fitting the experimental results Havriliak-Negami equation was used 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.

3. RESULTS AND DISCUSION

The real part of dielectric constant of investigated mixture for frequency 1kHz is shown in Fig. 1. It reflects phase sequence in cooling process. It can be seen that in the temperatures near phase transition SmC*-SmA*, the dielectric constant changes dramatically, which suggests that the strong relaxation processes in this temperature range occur (weaker the soft mode in the SmA* phase and stronger the Goldsone mode in ferroelectric the SmC* phase).

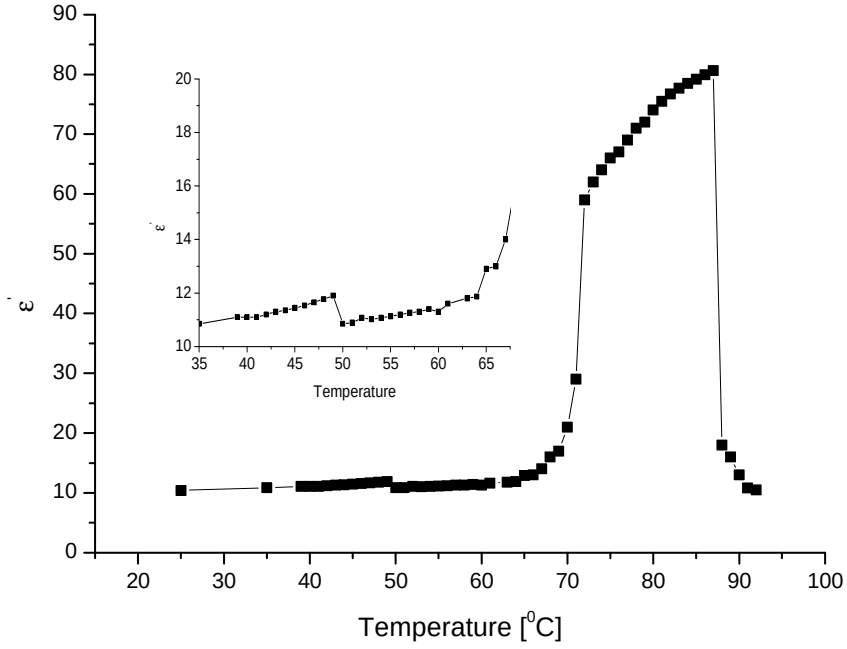


Fig. 1. Real part of dielectric permittivity vs. temperature for the whole temperature range investigated at 1kHz frequency

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:

$$SmA^{*} \rightarrow 88^{0}C \rightarrow SmC^{*} \rightarrow 65^{0}C \rightarrow Sm\,C_{A}^{*} \rightarrow 50^{0}C \rightarrow SmX\ .$$

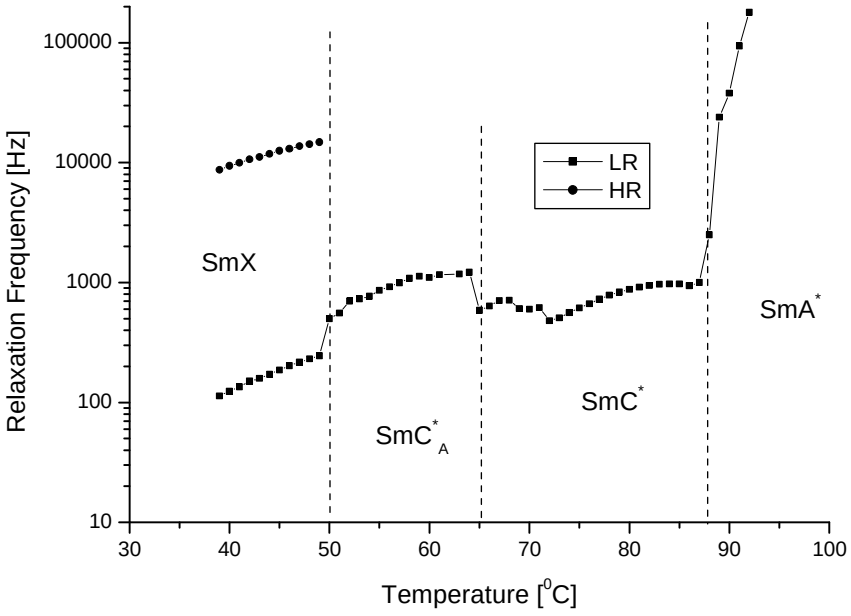


Fig. 2. Relaxation frequency of relaxation processes obtained on cooling for the whole temperature range

The relaxation processes registered in the low frequency region are related to the Maxwell-Wagner relaxation [7] and are not presented because this is a typical cell relaxation process.

The dielectric parameters obtained from Havriliak-Negami equation were calculated separately for each phase detected i.e. fitted into single or double relaxation modes in the particular case. The obtained results are shown in Fig. 2 and Fig. 3.

During cooling of the liquid crystalline sample from the isotropic liquid to the SmA* phase, the first relaxation process detected occurs in the vicinity of the phase transition to the ferroelectric phase and it is the soft mode. In the investigated mixture at 92^{o}C in the SmA* phase the soft mode was detected. Fitting experimental results to Havriiak-Negami equation gives dielectric strength and relaxation frequencies of the soft mode.

The first relaxation peak detected in the SmA* phase at 92^{o}C have relaxation frequency about 75kHz with the low dielectric strength about 3. The relaxation frequency decreases to about 20kHz and dielectric strength grows to

about 11 in the phase transition, temperature of which could be detected at 88^{O}C. At another side of the phase transition (in the SmC*) no soft mode was detected because it is covered by a Goldstone mode. This is a typical temperature dependence of soft mode without bias electric field [8].

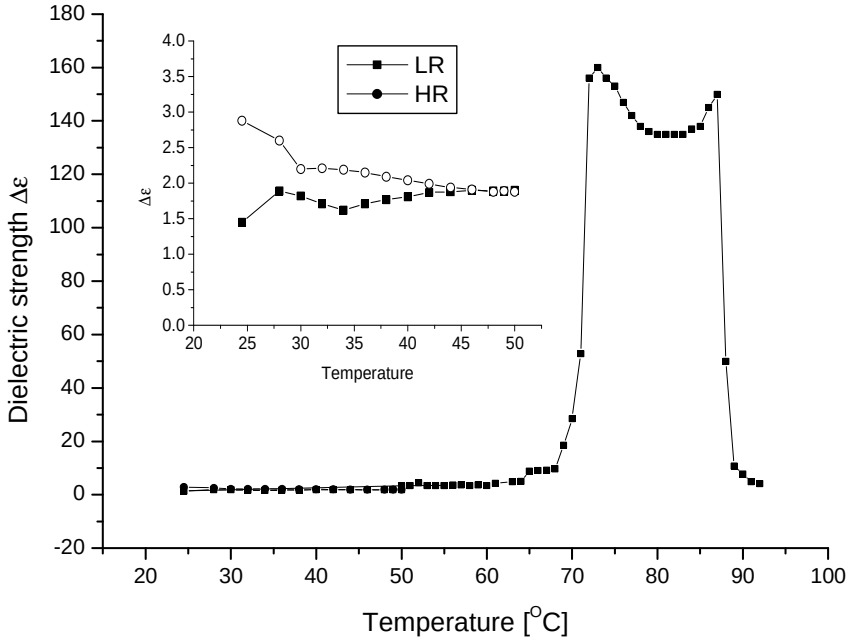


Fig. 3. Dielectric strength of the relaxation processes obtained on cooling vs. temperature

The next relaxation process appears in cooling below 88^{O}C, it is Golstone mode with the dielectric strength up to 175. The Goldstone mode is characteristic of collective molecular fluctuation for ferroelectric SmC* phase. The relaxation frequency of this mode changes in the investigated mixture from about 1kHz at 86^{O}C to 600Hz at 65^{O}C. At 72^{O}C on cooling the dielectric strength goes down rapidly up to 10 at 65^{O}C.

The SmC*$_{A}$ phase is the next one which appears on further cooling. Only one relaxation mode was detected in this phase. The temperature dependence of parameters of this mode is presented in Figs.2,3,4. The relaxation frequency changes from 1.2 kHZ at 64^{O}C up to 0.5 kHz at 50^{O}C and is rather low as for the SmC*$_{A}$ phase. This relaxation process shows fluctuations of relaxation frequency and the dielectric strength with temperature. It suggests that the antiferroelectic phase is not perfectly aligned. The activation energy of this process calculated in the

temperature range 50^{O}C-60^{O}C is equal 0.86 eV and is lower than obtained in [4,9]. This relaxation process is probably one of the collective modes existing in the 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 [8,9].

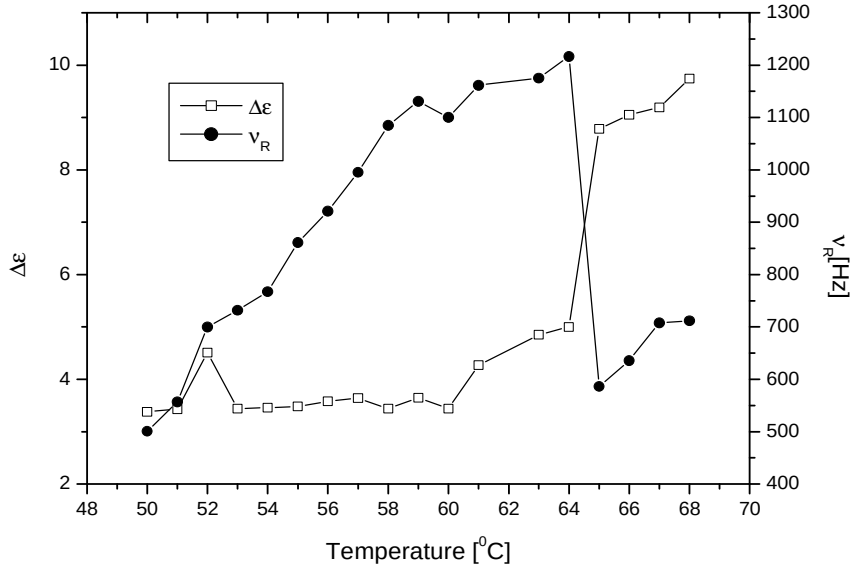


Fig. 4. Dielectric strength and relaxation frequency of the mode registered in the SmC*A phase vs. temperature

During cooling below 50^{O}C down to room temperature two weak relaxation processes were detected (see Figs. 2,3,5). The relaxation frequency of the high frequency process (HR) changes from 40 kHz at 50^{O}C to about 2kHz at room temperature. The dielectric strength is about 2 and grows with decreasing temperature. The relaxation frequency of the low frequency process (LR) changes with temperature from about 0.8 kHz at 50^{O}C down to 20 Hz near the room temperature. The dielectric strength of LR process is about 2 and decreases with decreasing temperature. Arrhenius plots were made for both relaxation processes. The obtained activation energies are rather high for both modes, for LR was equal to 1.24eV and for HR equal to 1.17eV.

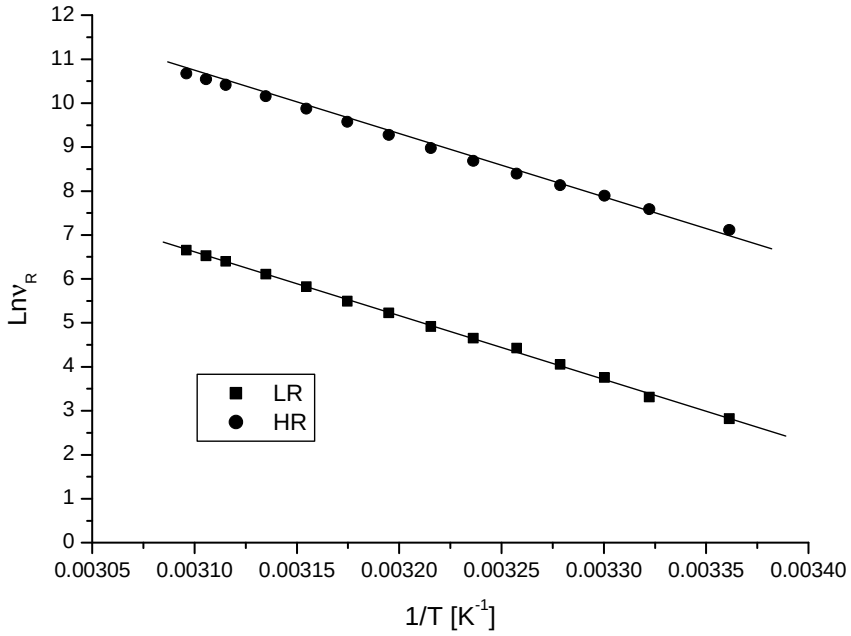


Fig. 5. Arrhenious plot for both relaxation processes detected in the SmX phase

It has been reported [11] that in antiferroelectric liquid crystalline materials SmI* and SmI*$_A$ phases can exists. The SmI* and SmI*$_A$ are the hexatic version of ferroelectric and aniferroelectric phases, respectively. The SmI* phase occurs in cooling process below the SmI*$_A$. Kundu et. al.[12] analyzing dielectric behaviour of antyferroelectric material have shown both mentioned phases i.e. separate dielectric relaxation process related to each phase. Mikułko et. al. [13] obtained two relaxation process in the SmI* phase with very high activation energy. Comparing these results [12,13] with these obtained in the present work one can see a lot of qualitative differences between relaxation frequencies and dielectric strength of detected relaxation processes, but detection of two relaxation processes as in [13] can suggests that in our case SmX phase could be interpreted as SmI* phase.

4. CONCLUSIONS

1. The temperature dependence of dielectric constant and dielectric characteristics of the investigated mixture proves the existence of a new phase (SmX) in the phase diagram in cooling process.
2. The soft mode parameters were obtained in the SmA* only.
3. In the SmC* phase the strong Goldstone mode was observed.
4. In the antiferroelectric SmC^*_A phase 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).
5. In the SmX phase two relaxation processes were obtained. These processes are Arrhenious-like with similar activation energes equal to about 1.2 eV. The new SmX phase may be SmI* phase, though the suggestion requires further investigations.

REFERENCES

[1] **Lagerwall J.P.F., Rudquist P., Lagerwall S.T., Gieβelmann F**., Liq. Cryst., **30** (2003) 399.
[2] **Brock J.D., Birgeneau R.J., Lister J.D., Aharony A.,** Phys. Today **7** (1989) 52.
[3] Mikułko A., Marzec M., Ossowska-Chruściel M.D., Chruściel J., Wróbel S., Ferroelectrics **343** (2006) 209.
[4] **Wojciechowski M., Bąk G.W., Tykarska M.,** Opto-electronic Rev. **16** (2008) 257.
[5] **Wojciechowski M.**, Sci.Bull. Tech. Univ. Lodz. No.1010, Phys., **28** (2007) 105.
[6] **Skrzypek K., Tykarska M.,** Ferroelectrics, **343** (2006) 177.
[7] **Wojciechowski M., Gromiec L.A., Bąk G.W**., J. Mol. Liquids, **124**, (2006) 7.
[8] **Buivydas M., Gouda F., Lagerwall S.T., Stebler B**., Liq. Cryst., **18** (1995) 879.
[9] **Pandey G., Dhar R., Agraval V.K., Dąbrowski R**., Ferroelectrics **343** (2006) 139.
[10] **Pandey M.B., Dhar R., Agrawal V.K., Dąbrowski R., Tykarska M**., Liq. Cyst. **31** (2006) 973.
[11] **Matsumodo T., Fucuda A., Johno M., Motoyama Y., Yuti T., Seomun S., Jamashita M.,** J. mater. Chem. **9** (1999) 2051.
[12] **Kundu S., Ray T., Roy S.K., Dąbrowski R.,** Liq. Cryst., **31** (2004) 119.
[13] **Mikułko A., Douali R., Legrand Ch., Marzec M., Wróbel S., Haase W**., Ferroelectrics **343** (2006) 133.

DIELEKTRYCZNE CHARAKTERYSTYKI ANTYFERROELEKTRYCZNEJ MIESZANINY CIEKŁOKRYSTALICZNEJ

Streszczenie

W pracy przedstawiono dielektryczne charakterystyki ostatnio zsyntetyzowanej ciekłokrystalicznej mieszaniny z indukowaną fazą antyferroelektryczną i występującą fazą ferroelektryczną (związki ciekłokrystaliczne, z których sporządzono mieszaninę nie posiadają samodzielnie fazy antyferroelektrycznej). Badania dielektryczne przeprowadzono w komórce o złotych elektrodach i uporządkowaniu planarnym. Otrzymane temperaturowe zależności inkrementu dielektrycznego i częstości relaksacji występujących procesów relaksacyjnych pozwoliły je opisać i przypisać do poszczególnych faz. W temperaturach niższych od temperatur, w których występuje faza antyferroelektryczna, zarejestrowano dwa procesy relaksacyjne, które prawdopodobnie związane są z heksagonalną odmianą fazy smektycznej tzn. SmI*.