MAREK WOJCIECHOWSKI,[1,2] MARZENA TYKARSKA[3]

[1]Centre of Mathematics and Physics, Technical University of Łódź
 90-924 Łódź, Al.Politechniki 11, Poland
[2]Institute of Physics, Technical University of Łódź
93-924 Łódź, Wólczańska 219/223, Poland
[3]Institute of Chemistry, Military University of Technology
 Kaliskiego 2, 00-908 Warsaw, Poland

DIELECTRIC PROPERTIES
OF ANTIFERROELECTRIC LIQUID CRYSTAL
4F5Bi(2F)

Recently synthesized an antiferroelectric liquid crystal compound has been studied by means of dielectric spectroscopy. The dielectric measurements were carried out in a cell with gold electrodes at planar orientation. The characteristics of dielectric relaxation modes in all phases existing in the investigated compound are presented.

Keywords: antiferroelectric LC, dielectric relaxations, Goldstone mode.

1. INTRODUCTION

A antiferroelectric liquid crystals show chiral smectic phases (ferroelectric SmC* and antiferroelectric SmC*$_A$) as well as subphases (SmC$^*_\alpha$, SmC$^*_\beta$, SmC$^*_\gamma$) with different combinations [1]. In these phases and subphases collective molecular relaxation processes exist. Dielectric spectroscopy is useful tool for investigations of these relaxation processes. In the SmA* phase soft mode, related to collective tilt angle fluctuation of molecules, is registered [2-4]. In the SmC* phase soft mode is covered by strong Goldstone mode, thus only GM, with high amplitude, is measured without application of dc bias [2-5]. In the SmC*$_A$ phase two relaxation modes can be detected. Lower frequency mode observed in kHz region has been named as P_L mode, whereas the higher frequency mode observed at frequencies higher than 200 kHz has been named as P_H mode. The P_L mode is assigned to the in-phase and P_H mode to the anti-phase
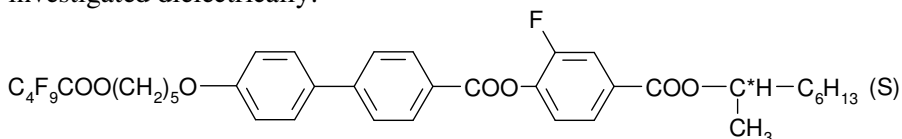
angle fluctuations of the directors of the antitilted molecules in successive layers, respectively [5-7].

The numerous dielectric investigations of new liquid crystals are carried out to search their dielectric characteristics, especially dielectric relaxation modes in the antiferroelectric phase, were the origin of the modes is still unsettled.

In this work the dielectric characteristics of recently synthesizes antiferroelectric liquid crystalline compound 4F5Bi(2F), studied in the cell with the gold electrodes, are presented and discussed. In the investigated compound the ferroelectric and antiferroelectric phase exists.

2. EXPERIMENTAL

Antiferroelectric liquid crystalline compound 4F5Bi(2F) presented below, with relatively broad temperature range of antiferroelectric phase, was investigated dielectrically:

$$C_4F_9COO(CH_2)_5O \text{—} \bigcirc\text{—}\bigcirc\text{—}COO\text{—}\bigcirc\text{—}COO\text{—}C^*H\text{—}C_6H_{13} \text{ (S)}$$

with F substituent on the third ring and CH_3 on the chiral carbon.

The investigated compound was synthesized in the Institute of Chemistry, Military University of Technology (Warsaw) [8].

The phases sequence in the investigated compound is as follows [8]:

$$Cr \rightarrow 43.6 \; SmC^*_A \rightarrow 101.3 \; SmC^* \rightarrow 105.5 \; SmA^* \rightarrow 109.9 \; Izo$$

The dielectric measurements were performed for the liquid crystal compound placed between two parallel glass plates with 5×5mm gold electrodes. We used standard cells, commercially available from AWAT. The used cells give planar orientation. The sample thickness was $d = 5\mu$m. 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.

The dielectric measurements were performed in cooling process of liquid crystal sample.

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.

The measurements of the helical pitch based on selective light reflection phenomenon, were carried out with the use of Shimadzu UV-VIS-NIR spectrometer in the range 360-3000 nm. The measurement of the helical pitch and helical twist sense in antiferroelectric phase were performer by methods described in [9].

3. RESULTS AND DISCUSION

As the first result we present a temperature dependence of dielectric permittivity at a constant frequency. We chose the 1 kHz frequency because the registered relaxation processes exist near this frequency region. Real part of dielectric constant of investigated compound for frequency 1 kHz is shown in Fig. 1, and reflects phase sequence upon cooling. Ferroelectric phase exists in the temperature range 105^0C-95^0C. In this phase there is a large contribution from the Goldstone mode. In the isotropic liquid phase the dielectric permittivity is practically constant $\varepsilon = 5.8$. a shift of dielectric constant to about $\varepsilon = 7$ is observed on cooling the sample to SmA* phase with weak growing tendency with decreasing temperature.

On further cooling it is seen that in the temperatures near phase transition SmC*-SmA*, the dielectric constant changes dramatically, which suggests that the strong relaxation process in this temperature range occurs. On further cooling an antiferroelectric phase appears with practically constant dielectric permittivity $\varepsilon = 4.8$ at 50^0C.

The dielectric parameters obtained from Havriliak-Negami equation were calculated separately for each of detected phase, i.e. fitted into single or double relaxation modes in the particular case. The obtained results for the ferroelectric phase and antiferroelectric phase are shown in Fig. 3 and Fig. 5 as examples.

During the cooling process of the liquid crystalline sample from isotropic liquid to the SmA* phase, the first detected relaxation process occurs in the vicinity of the phase transition to the ferroelectric SmC* phase.
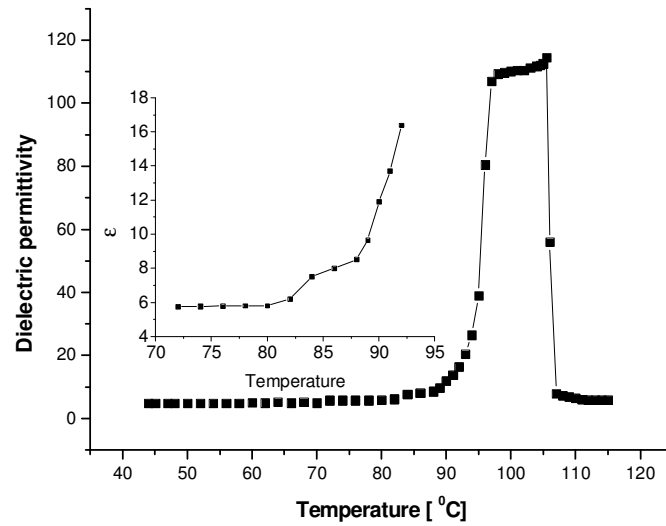
Fig. 1. Real part of dielectric permittivity vs. temperature for the whole temperature range investigated at the 1 kHz frequency
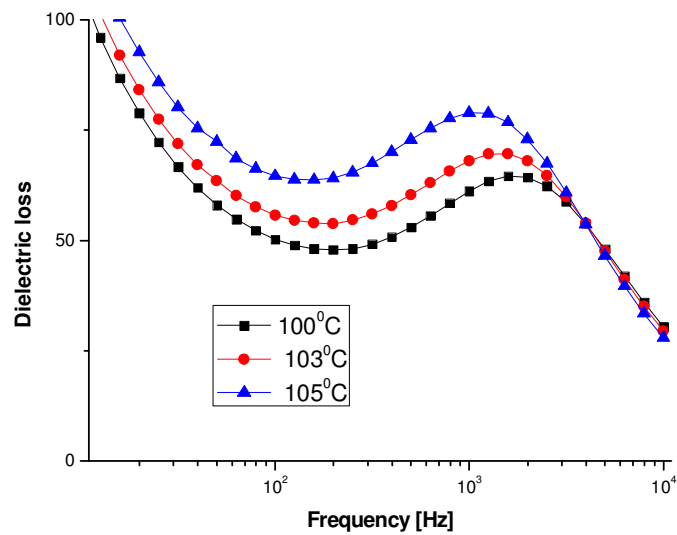

Fig. 2. Dielectric loss of Goldstone mode for chosen temperatures in the SmC* phase.

    In the investigated compound in the paraelectric SmA* phase a few points
of relaxation process were detected with relaxation frequency higher than
50 kHz and this process was assigned to soft mode i.e. director tilt fluctuation
of molecules in the smectic layers [2-4] and is not presented in this work.
    On cooling, ferroelectric Goldstone mode appears rapidly with strong
amplitude at the temperature 105.5^{0}C. This relaxation process is presented
in Fig. 2 for three temperatures chosen for ferroelectric phase. Goldstone
mode parameters are presented in Fig.6 and Fig. 7. The relaxation frequency
temperature dependence (Fig. 6) increases from about 1 kHz at 105^{0}C to the
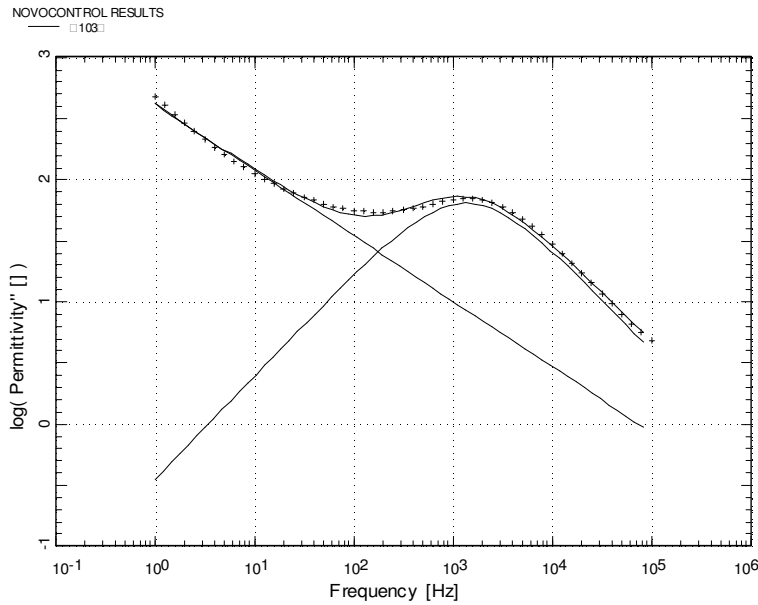about 2 kHz at 95^{0}C.

Fig. 3. Goldstone mode fitting to Havriliak-Negami equation. Havriliak-Negami
parameters at T = 103^{0}C: σ_0 = 4.1 10^{-8}[S/cm], n = 0.54, τ_{max} = 1.19·10^{-4}s,
$\Delta\varepsilon$ = 162, α = 0.85, β=1

    The dielectric strength of the Goldstone mode (Fig. 7) changes from about
$\Delta\varepsilon$ = 200 near the phase transition to the SmA* phase to about $\Delta\varepsilon$ = 24 at 95^{0}C.
The dielectric strength of GM has maximum at the temperature of phase
transition from SmA* phase and drops down with temperature to about $\Delta\varepsilon$ = 150
at the temperature 100^{0}C and then rapidly decreases to $\Delta\varepsilon$ = 24 at 95^{0}C.

In the vicinity of SmC*-SmC*$_A$ transition temperature the dielectric strength of the Goldstone mode decreases rapidly with decreasing temperature and is registered into SmC*$_A$ phase. It seems that GM penetrates into the SmC*$_A$ phase. This situation has been observed in several other liquid crystalline materials [4, 10]. Such penetration of Goldstone mode inside the SmC*$_A$ phase has been extended to few degrees, and for thin sample this expansion is even larger [11].
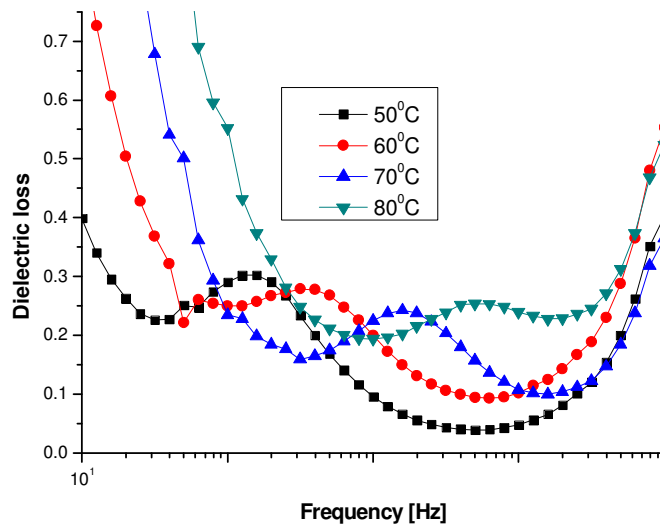

Fig. 4. Dielectric loss of AF mode at chosen temperatures

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 dielectric parameters of this mode is presented in Figs. 4-7. The relaxation peaks are presented in Fig. 4. for chosen temperatures in the range of antiferroelectric phase. One can see relatively large shift of dielectric loss peeks to lower frequency with decreasing temperature.

Temperature dependence of relaxation frequency is presented in Fig. 6. The relaxation frequency changes from about 2 kHz at 94 ^{0}C up to less than 70 Hz at 44^{0}C. Two different dependences of relaxation frequency (Fig. 6) are visible in this temperature range.
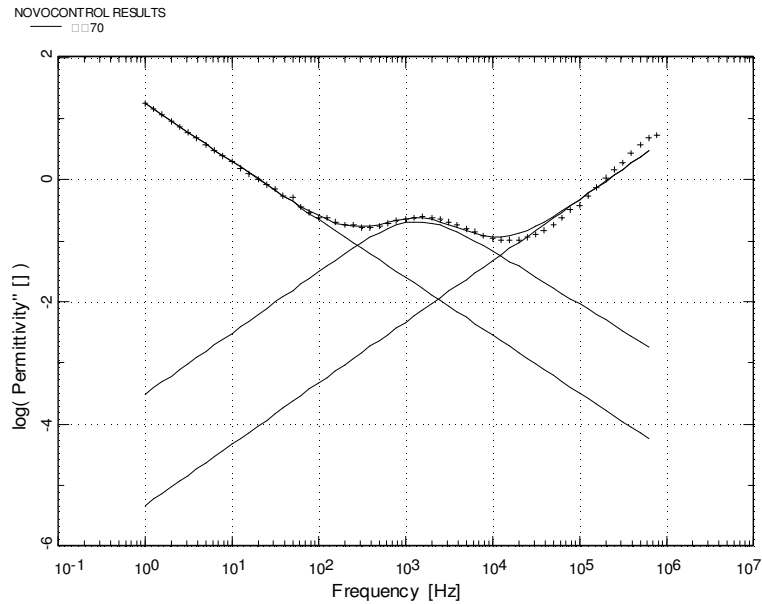
NOVOCONTROL RESULTS
——— 70

Fig. 5. AF mode fitting to Havriliak-Negami equation.Havriliak-Negami parameters of P_L mode at T = 70^{0}C: $\sigma_0 = 1.14 \ 10^{-11}$[S/cm], n = 0.95, $\tau_{max} = 1.15 \cdot 10^{-4}$s, $\Delta\varepsilon = 0.58$, $\alpha = 1$, $\beta = 0.88$
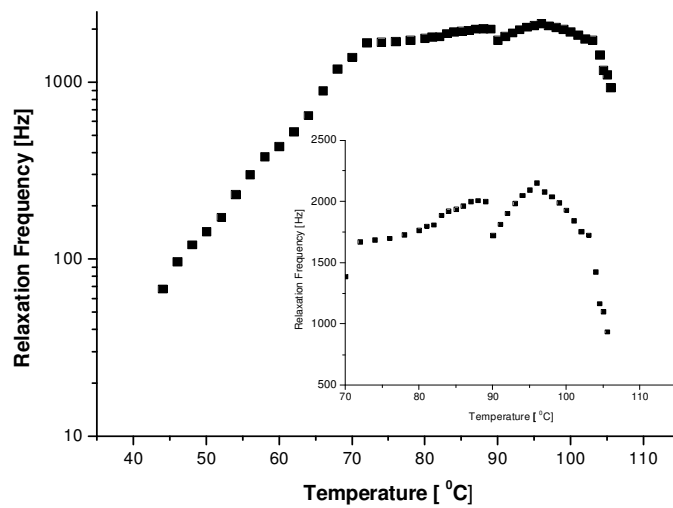

Fig. 6. Dielectric relaxation frequency of the mode registered in the investigated compound vs. temperature.

In the lower temperature region of the SmC*$_A$ phase (75^{0}C-44^{0}C) the relaxation frequency changes from about 1.5 kHz at 75^{0}C to above 70 Hz at 44^{0}C, the dielectric strength is constant $\Delta\varepsilon = 0.6$. This frequency range of relaxation process observed in the SmC*$_A$ phase is lower than obtained for other antiferroelectric materials [6, 12], but it is in a good agreement with lower frequency mode observed in the work [13] (between 50 Hz and 50 kHz) for 4F6Bi compound.

The relaxation frequency of the relaxation mode observed in the low temperature part of antiferroelectric phase strongly follows the Arrhenius behaviour. According to the Arrhenius equation, a plot of $\ln\nu_R$ vs. 1/T should be straight line, the least square fit gives activation energy $\Delta E_A = 1.04$eV, Fig. 8.

This result is in good agreement with: $\Delta E_A = 1.2$ eV [14], $\Delta E_A = 1.04$ eV calculated from [15], $\Delta E_A = 1.1$eV calculated from [10], $\Delta E_A = 0.98$ eV [16], $\Delta E_A = 1.3$ eV [17] for low frequency mode observed in antiferroelectric state.
Thus the relaxation process observed in investigated compound should be 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, 10-17].

In the high temperature region (94^{0}C-76^{0}C) the relaxation frequency changes from about 2 kHz at 94^{0}C to above 1.5 kHz at 76^{0}C. The relaxation process shows some fluctuations of relaxation frequency with temperature in this temperature range. As it is shown in Fig. 7, in this temperature range the dielectric strength of the relaxation mode changes from $\Delta\varepsilon = 17$ at 94^{0}C to $\Delta\varepsilon = 0.6$ at 76^{0}C. In this mode the relaxation frequency is low (2 kHz), dielectric strength is changeable and the temperature dependence of relaxation frequency shows inhomogeneity thus it cannot be recognized as a high relaxation mode observed in the antiferroelectric state [7, 10].

One of the possibility is that in this temperature range ferrielectric subphase SmC*γ exists. In this subphase low relaxation mode (about 4 kHz) decreases its dielectric strength sharply with the decrease of temperature whereas only small variation of the relaxation frequency with temperature is found [18]. In our dielectric results we have similar situation.

Additionally a helical pitch measurement of the tested compound was performed. These measurements based on selective light reflection phenomenon, with the use of UV-vis-NIR Spectrophotometer in the wavelength range 360 nm-3000 nm, in the SmC*A phase, did not give any results.
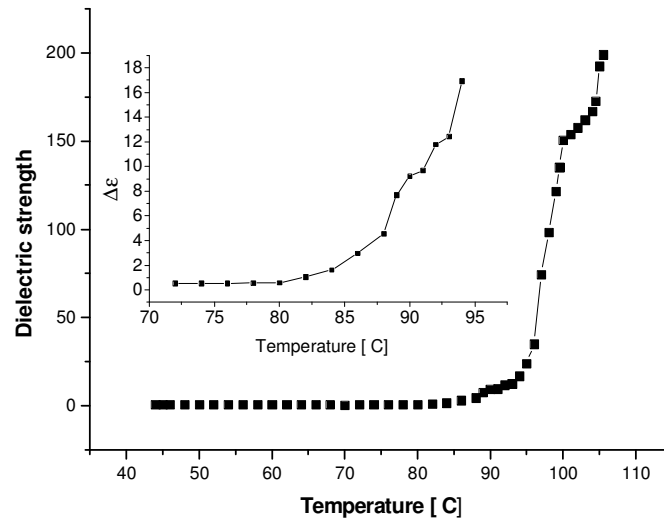
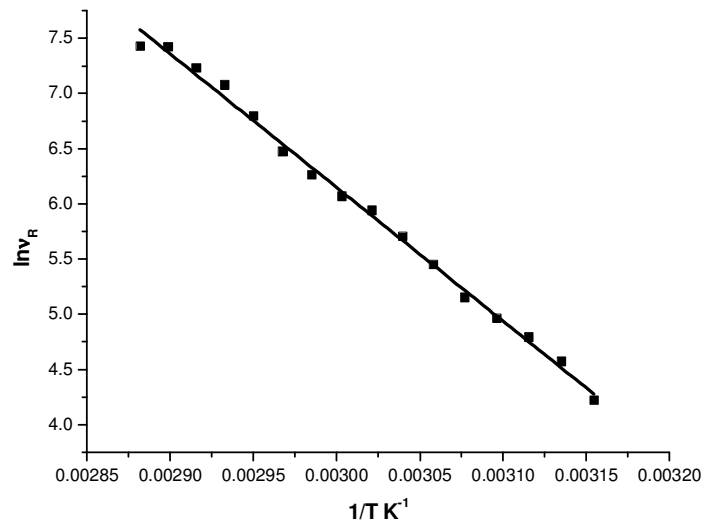Fig. 7. Dielectric relaxation frequency of the mode registered in the investigated compound vs. temperature

Fig. 8. Arrhenius plot of the antiferroelectric P_L mode detected in the lower temperatures of SmC*$_A$ phase

It means that the helical pitch is over 2 μm. Thus, the helical pitch and twist sense were established by the microscopic observation of contact sample with the standard compound 4F6Bi [9, 19]. It was found that the helical structure of antiferroelectric phase is left handed and the helical pitch is high but it even increases with the decrease of the temperature. It is worth noting that, the increase of the helical pitch, observed as the increase of the brightness of the texture, starts around 75^0C.

The higher temperature phase (75-95^{0}C) cannot be SmC*$_\gamma$ because its helical pitch is usually higher than the pitch of antiferroelectric phase [20].

The dielectric investigations of a compound being analogous of MHPOBC but substituted laterally with the chlorine atom made by Pandey et al. shows that a new type of polar phase exists between SmC*$_\gamma$ and SmC*$_A$ phases [18]. This phase was designed as SmC*$_x$. In the dielectric mode observed in this phase, the dielectric strength increases with decrease temperature. Its relaxation frequency is about 4 kHz. The decrease of dielectric strength in the SmC*$_x$ phase, occurs due to the decrease in ferroelectric order or increase in antiferroelectric order with decrease temperature [18]. Similar situation is observed in the temperature range (75-95^{0}C) in the investigated compound 4F5Bi(2F). Thus in our case, the observed relaxation mode could be related to the SmC*$_x$ phase as in work [18]. It is worth noting that we observed some coincidence in dielectric and optical results. The microscopic observations shown detectable increase of the helical pitch at 75^{0}C. The dielectric results shown good stabile ordering of SmC*$_A$ at this temperature.

CONCLUSIONS

1. The dielectric study shows, that recently synthesized 4F5Bi(2F) compound, goes into three different liquid crystalline phases: parraelectric SmA*, ferroelectric SmC*, antiferroelectric SmC*$_A$ on cooling process.
2. In the SmC* phase the strong Goldstone mode (maximum dielectric strength about 200) was observed. The Goldstone mode is observed at about 5^{0}C into SmC*$_A$. This phason mode exists due to the fluctuation of the phase angle.
3. In the SmC*$_A$ phase only one dielectric relaxation mode was detected.
4. In the lower temperature range of 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) with activation energy ΔE_A = 1.04 eV.

5. The relaxation process observed in the higher temperature range (75-95^{0}C) could be interpreted as a representative of a new type of smectic polar phase (SmC*$_x$) [18].

REFERENCES

[1]   **Lagerwall J.P.F., Rudquist P., Lagerwall S.T., Gieβelmann F**., Liq. Cryst., **30** (2003) 399.

[2]   **Buivydas M., Gouda F., Andersson G., Lagerwall S.T., Stebler B., Bomelburg J., Heppke G., Gestblom B.**, Liq. Crystals, **23**, (1997) 723.

[3]   **Merino S., De Daran F., De La Fuente M.R., Jubindo M.A.P., Sierra P**., Liq. Cryst., **23** (1997) 275.

[4]   **Kumari S., Das I.M.L., Dąbrowski R**., J. Mol. Liquids, **158** (2011) 1.

[5]   **Kumar A., Prakash J., Biradar A.M.,** Liq. Cryst., **37** (2010) 247.

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

[7]   **Pandey G., Dhar R., Agraval V.K., Dąbrowski R**., Ferroelectrics **343** (2006) 139

[8]   **Gasowska J., Dabrowski R., Drzewinski W., Kenig K., Tykarska M., Przedmojski J.**, Mol. Cryst. Liq. Cryst. **411** (2004) 231.

[9]   **Tykarska M., Czerwiński M., Miszkurka J**., Liq. Cryst., **37** (2010) 487.

[10] **Kumar A., Dhar R., Agrawal V.K., Dąbrowski R**., Phase Transitions, **80** (2007) 231.

[11] **Ray T., Kundu S., Majumder P.T., Roy S.K., Dąbrowski R**., Mol. Liquids., **139** (2008) 35.

[12] **Pandey G., Dhar R., Agraval V.K., Dąbrowski R**., Phase Trans. **12** (2004) 1111.

[13] **Dwivedi A., Dhar R., Pandey M.B., Das I.M.L., Dąbrowski R**., J. Mol. Liquids, **148** (2009) 1.

[14] **Fąfara A., Marzec M., Wróbel S., Dąbrowski R., Haase W**., IEEE Trans. Dielectr. Electr. Insul., **8** (2001) 477.

[15] **Pandey M.B., Dhar R., Agrawal V.K., Dąbrowski R., Tykarska M**., Liq. Cryst. **31** (2006) 973.

[16] **Wojciechowski M., Bąk G.W., Tykarska M**., Opto-Electronics Rev. **16** (2008) 257.

[17] **Bhattacharyya S.S., Rahman M., Mukherjee A., Wu S.L., Chaudhuri B.K**., Appl. Phys. **9** (2009) 390.

[18] **Pandey G., Dhar R., Dąbrowski R**., Ferroelectrics **343** (2006) 83.

[19] **Tykarska M**., Mol. Cryst. Liq. Cryst., **449** (2006) 79.

[20] **Takezoe Li.J., Fukuda H**., A. Jpn. J. Appl. Phys. **30** (1991) 536.

WŁASNOŚCI DIELEKTRYCZNE ANTYFERROELEKTRYCZNEGO CIEKŁEGO KRYSZTAŁU 4F5Bi(2F)

Streszczenie

W pracy przedstawiono dielektryczne charakterystyki ostatnio zsyntetyzowanego antyferroelektrycznego ciekłego kryształu o szerokim zakresie fazy antyferroelektrycznej. Badania dielektryczne przeprowadzono w komórce o złotych elektrodach i uporządkowaniu planarnym. Przedstawiono temperaturowe zależności inkrementu dielektrycznego i częstości relaksacji występujących procesów relaksacyjnych. W fazie ferroelektrycznej zarejestrowano silny mod Goldstone'a. W fazie antyferroelektrycznej zarejestrowano dwa procesy relaksacyjne i przedstawiono ich interpretacje w oparciu o dodatkowe pomiary skoku spirali badanego związku.