SCIENTIFIC BULLETIN OF THETECHNICAL UNIVERSITY OF LODZ
No. 1082 Physics, Vol. 31 2010

MAREK WOJCIECHOWSKI[1,2]

[1] Center of Mathematics and Physics, TechnicalUniversity of Łódź
90-924 Łódź, Al. Politechniki 11, Poland
[2] Institute of Physics, TechnicalUniversity of Łódź, Wólczańska 219
90-924 Łódź, Poland, e-mail: marekw@p.lodz.pl

DIELECTRIC PROPERTIES OF FERRIELECTRIC PHASE INDUCED IN LIQUID CRYSTAL MIXTURE

Mixtures of two liquid crystalline compounds (which do not exhibit antiferroelectric phases separately) showferrielectric phase in a broad temperature range in 5:5 and 3:7 compositions. The dielectric spectroscopy technique was used for investigation of collective molecular motions in these mixtures. Two relaxation modes were detected in the ferrielectric phase. The temperature dependence of the parameters of the dielectric relaxation modes of ferrielectric phase are compared and discussed.

Keywords: Ferrielectricphase, Goldstone mode.

1. INTRODUCTION

Antiferroelectric liquid crystalline compounds show not only antiferroelectic and ferroelectric phases, but also some kind of chiral smecticsubphases. The ferrielectricsubphases appear as a result of competition between synclinic ordering in ferroelectric phase and anticlinic ordering characteristic for the antiferroelectric phase. The notation proposed by Lagerwall [1] is used to mark phases and subphases in antiferroelectric compounds. The structure of chiral smecticsubphases could be described by the clock model [2] with three- and four-layer unit cell for and $\mathrm{Sm}C^*_\beta$ phases respectively. The $\mathrm{Sm}C^*_\beta$ as the $\mathrm{Sm}C^*_A$ phase has an antiferroelectric nature [3], but in contrast to the $\mathrm{Sm}C^*_\gamma$ whichis ferroelectric nature. The unit cell of ferrielectric $\mathrm{Sm}C^*_\gamma$ consists of two synclinic and one

anticliniclayers which give net electric polarization, but lower than in the ferroelectric phase [2]. However, the exact structure of the repeating unit is not clear until now [1]. The $\mathrm{Sm}C^*_\gamma$ exhibits one polar mode with low relaxation frequency, which indicates that the response is due to collective fluctuations in the phase angle, e.g. a distortion of the $\mathrm{Sm}C^*_\gamma$ helix [1]. In this phase, ferrielectric Goldstone mode was detected but in some cases two dielectric relaxation modes were observed [4-7] or one dielectric mode [8]. Recently, S. Gosh et al. [9] observed three relaxation modes in this phase.

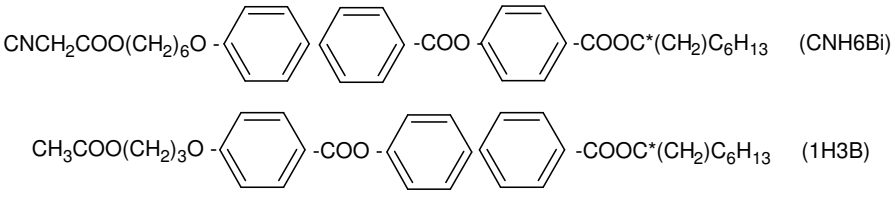
Broadband dielectric spectroscopy has often been used to study the molecular and collective molecular relaxations in ferroelectric liquid crystalline materials. The experimental data concerning the dielectric relaxation modes, especially in ferrielectricsubphases, are still needed.

The dielectric properties of two compositions (5:5) M1[10,11] and (3:7) M3[12] of a binary mixture of liquid crystalline compounds has been studied earlier. The investigated mixtures possess a ferrielectricsubphase over a broad temperature interval.

In this work the dielectric characteristics of ferrielectric phase of these mixtures are compared and discussed. Additionally, new dielectric measurements were made for M3 mixture and are added for discussion.

2. EXPERIMENTAL

The mixtures of compositions 5:5 mole ratio (M1) and 3:7 (M3) of liquid crystalline compounds presented below (which do not exhibit antiferroelectric phase separately) werestudied. The molecular structure of the components is presented below:



The investigated compounds were synthesized and the mixtures were prepared in the Institute of Chemistry, Military University of Technology (Warsaw, Poland). The phase sequences for the two compounds are as follows:

Cr→SmA*→Iso for 1H3B and Cr→SmC*→SmA*→Iso for CNH6Bi [13]. The phase sequences in the investigated mixturesare [13]:

M1

$$Cr \rightarrow Sm\,C_A^* \rightarrow 38 \div 41^0C \rightarrow Sm\,C_\gamma^* \rightarrow 66 \div 67.5^0C \rightarrow SmA^* \rightarrow 103^0C \rightarrow Is$$

M3

Cr 18-19.5°C→SmC*$_\gamma$→52°C→SmA*→105°C→I

The dielectric measurements were performed for the liquid crystal mixtures placed between two parallel glass plates with 5x5 mm gold electrodes. The sample thickness was d = 5 μm. We used standard cells, commercially available from AWAT Warsaw. The cells used give planar orientation. The measurements were carried out with Solartron 1260 A Impedance Analyser with Chelsea Dielectric Interface in the frequency range 10^{-1} Hz÷$5 \cdot 10^5$ Hz. The measuring sinusoidal signal (0.1 V) was applied nearly perpendicularly to the director of smectic layers. The measurements for different DC bias fields were made to analyze obtained dielectric relaxation modes.

For fitting the experimental results the Havriliak-Negami equation in the following versionwas used:

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

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

All the presented experimental results were obtained during cooling.

3. RESULTS AND DISCUSION

The ferrielectric $Sm\,C_\gamma^*$ subphase have been detected dielectrically in two compositionss 5:5 M1[10,11] and 3:7 M3[12] of the investigated mixture, in relatively broad temperature range. In the M1 mixture two relaxation processes were observed in the whole temperature range of the phase. In the M3 mixture two relaxation processes were detected in the lower part of the temperature range of this phase, but only one at higher temperatures. Additionaly, the higher relaxation process observedat higher and lower temperatures in the M3 mixture show differences in the temperature characteristics of dielectric parameters. The comparison of dielectric parameters of the same kind of ferrielectricsubphase in

M1 and M3 mixture will be shownand discussed together with dielectric measurements for new sample of mixture M3. The results obtained for M3 [10] are marked M3No1and a new results are marked as M3No2.

3.1. Dielectric relaxation modes

In the M1 mixture two dielectric relaxation modes were detected in the frequency range: at 18-30 kHz HFM (high frequency mode) and at 1-6 kHz LFM (low frequency mode). Both peaks are well defined in the whole temperature range of chiral smectic C* subphase [11] and interpreted as a ferrielectricsubphase [12]. In the M3No1 mixture in the temperature range between 25°C and 52°C the ferrielectric $\mathrm{Sm}\,C^*_\gamma$ subphaseis observed in the cooling cycle and shows two different temperature dependencies of the dielectrics parameters of relaxation modes, in the lower temperature region and in the higher temperature region [12].

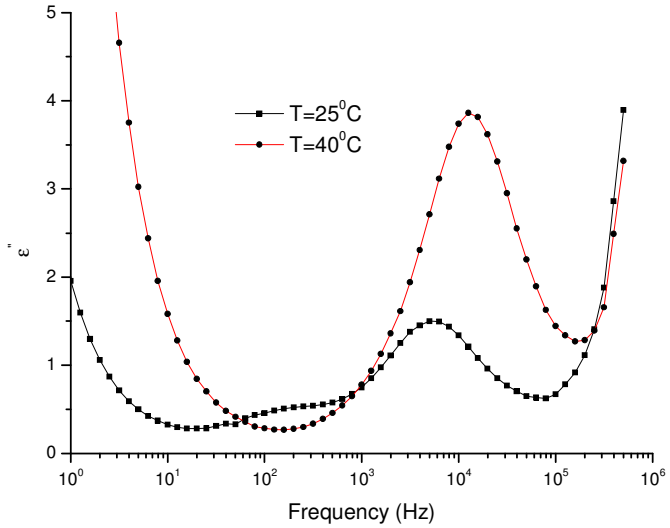


Fig. 1. Imaginary part of the dielectric spectrum of the M3No1 mixture at chosen temperatures in which one or two relaxation modes were registered in the ferrielectric phase

In the lower temperature range between 25°C and 35°C two relaxation processes are observed in the $\mathrm{Sm}\,C^*_\gamma$ subphase [12], but at higher temperatures

35°C-52°C, only one relaxation peak is detected. The dielectric response in these two temperature regions is shown in Fig. 1. At temperature 27°C one can see two relaxation processes: the first one in the 100 Hz region and the second one in the k Hz region and only one mode at temperature 40°C (high temperature region).

Mixture M3No2, the same mixture mentioned above, but new sample prepared in the same way gives different dielectric response i.e.two relaxation modes in the whole temperature range of ferrielectric phase (as shown in Fig. 2) at temperatures representing two temperature regions as in Fig. 1 contrary to M3No1 Fig. 2 show two peaks in the temperature 40°C.

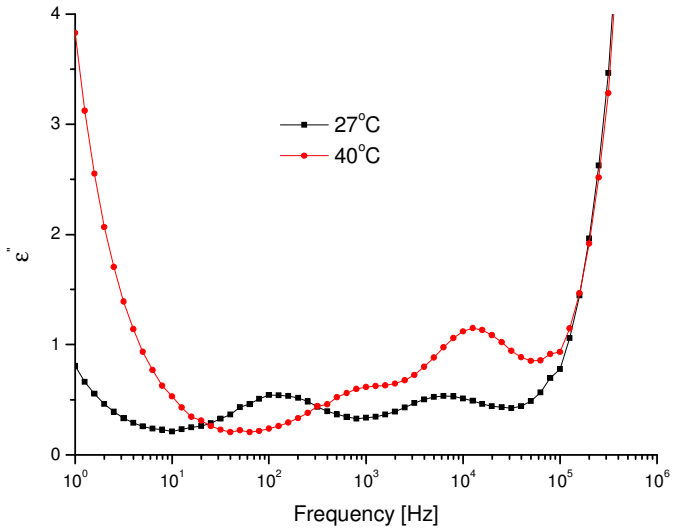


Fig. 2. Imaginary part of the dielectric spectrum ofthe M3No2 mixtureat chosen temperatures as in Fig. 1, here two relaxation modes were registeredin the ferrielectric phase in whole temperature range of phase existing

The experimental results show that in the ferrielectric $\mathrm{Sm}\,C^*_\gamma$ subphaseit is possible to obtain one or two relaxation modes in the M3 mixture.

3.2. Relaxation frequency

The relaxation frequency ν_R and the dielectric strength $\Delta\varepsilon$ of the relaxation modes were obtained by fitting the experimental results with Havriliak-Negami

equation. An example of the fitting procedure for the low-frequency mode (LFM) and high-frequency mode (HFM) in lower temperature region is presented in Fig. 3 for the sample M3No.2 code.

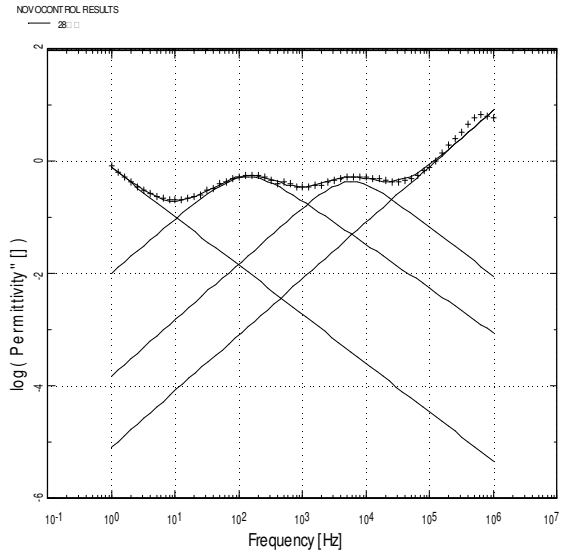


Fig. 3. Fitting procedure to Havriliak-Negami equation for two peaks observed at 28°C in the ferrielectric phase of M3No2 mixture

The values ν_R obtained from the fittings are presented in Fig. 4-6 for M1, M3No1 and M3No2 mixtures respectively.

In the M1 mixture two dielectric relaxation modes were detected in the frequency range at 18-30 kHz (HFM) and at (1-6) kHz(LFM).

The relaxation frequency changes from 200 Hz up to about 800 Hz with the temperature increasing from 25°C up to 32°C for the LFM mode of M3No1 mixture.The relaxation frequency of the HFM mode changes from 6 kHz up to about 10 kHz in the same temperature range. In the high temperature range, where LFM disappear i.e. in the temperature range between 35°C and 52°C only the HFM mode was observed. The relaxation frequency of the HFM mode in this temperature range increases from about 10 kHz at 35°C to about 50 kHz near phase transition to SmA* phase.

In the M3No2 mixture two dielectric modes were detected in the whole temperature range of $\mathrm{Sm}C^*_\gamma$ subphase. The LFM changes from about 100 Hz at 27°C to about 1.6 kHz at 47°C and HFM changes from 5.5 kHz to 34 kHz at the same temperature interval.

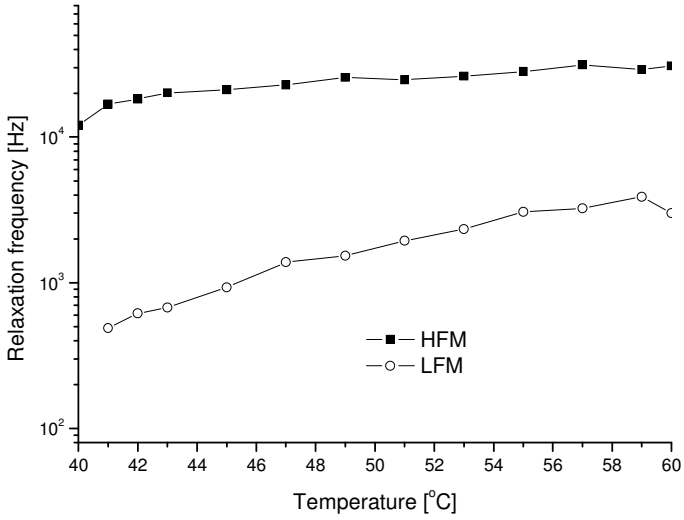


Fig. 4. Temperature dependence ofthe relaxation frequencies of ferrielectric phase in M1 mixture

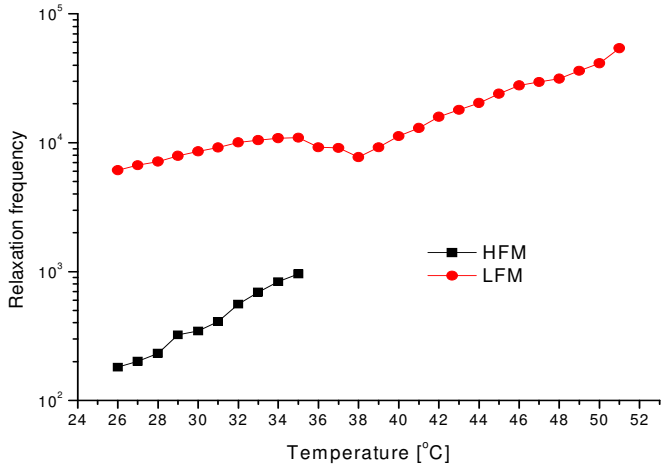


Fig. 5. Temperature dependence of the relaxation frequencies in the ferroelectric phase of M3No1 mixture

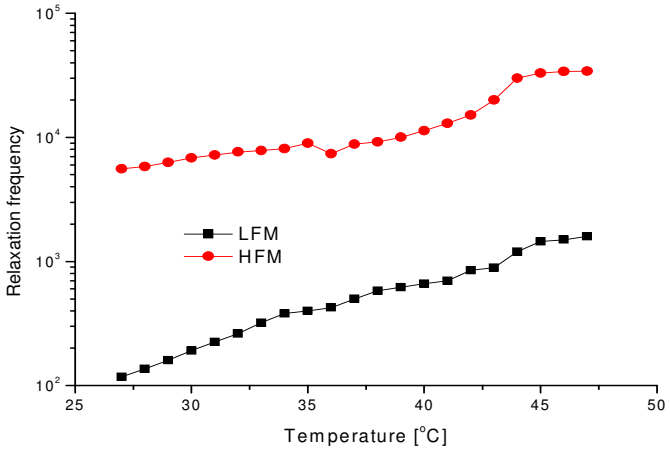


Fig. 6. Temperature dependence of the relaxation frequency in the ferroelectric phase of M3No2 mixture

The LFM mode shows a little higher relaxation frequency in the M1 mixture than in the M3 mixtures. The comparison show additionally that the relaxation mode can disappear in higher temperatures. The LFM mode observed in the investigated mixtures in the frequency region 100 Hz is similar to SLM (surface layer mode) observed by Bourny et al. [5] and Sarmento et al. [6]. Theseauthors suggest that this relaxation process is apparently related to the existence of visible disclination lines. Unfortunately,it is not possible to observe the disclination lines in our case due to gold electrodes used. However both, relaxation frequency range and that the mode is registered in ferrielectric phase suggest that we observe the surface layer mode.The $\mathrm{Sm}C^*_\gamma$ is extremely sensitive to cell conditions [9], in thin samplesthe surface effect dominates. The SLM is similar to the domain mode (DM) [14,15] induced by DC bias, related to formation ferroelectric domains in the bulk and surface after the helix unwinding. The frequency of DM is lower than that of the GM and less than 1 kHz and depends on the sample thickness.

The comparison of values of relaxation frequency of HFM and its temperature dependence show that for all mixtures relaxation frequency is at the order of 10 kHz and additionally in M3 mixtures the same changes in temperature tendency are observed.

The possible interpretation of HFM mode is that it is a collective relaxation mode related to phase angle fluctuation, i.e. a distortion of the $\mathrm{Sm}C^*_\gamma$ helix [1,8,9], so called ferrielectric Goldstone mode (GM).

Kundu et al. [7] found only one dielectric relaxation mode, in kHz region, due to the ferrielectric GM in the $\mathrm{Sm}C^*_\gamma$.

Pandey et al. [8] observed two dielectric modes in the $\mathrm{Sm}C^*_\gamma$, one at about 5 kHz interpreted as ferrielectric GM and the second at about one decadehigher frequency . The same modes existed in higher temperatures in the SmC* phase.

Ghosh et al. [9] observed three dielectric modes in this phase. Two in the low frequency region and one in the megahertz region. The lowest frequency mode, which was observed around 350 Hz can be assigned as a ferrielectric GM, while the other, observed at around 2 kHz was interpreted as a classic ferroelectric GM. The third mode in the high frequency region was related to antiferroelectric ordering in the ferrielectric phase.

Above examples suggest that HFM in all investigated mixtures can be assigned to ferrielectric GM.

3.3. Activation energy of the relaxation modes

The Arrhenius plots of three investigated mixtures were made and are shown in Figs. 7÷9.

In the M1 mixture (see Fig. 7) the Arrhenius plots clearly show two relaxation processes with two different activation energies. The activation energy for LFM is about 4 times higher than for HFM. LFM has higher activation energy than LFM for all mixtures.In the M3 mixture the situation is more complicated and differs for M3No1 and M3No2. The Arrhenius plots suggest that we have to do with three relaxation processes. The HFM changes its temperature dependence at about 35°C and has two activation energies. This situation take please only for the M3 mixtures.

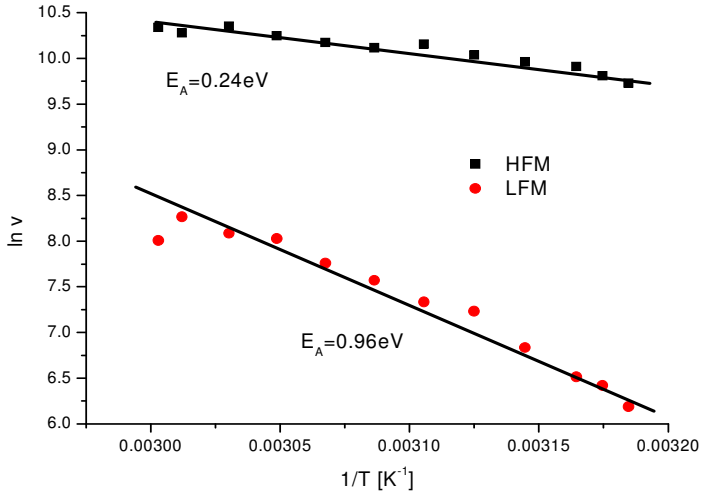


Fig. 7. Arrhenius plots for the mixture M1 investigated earlier [11]

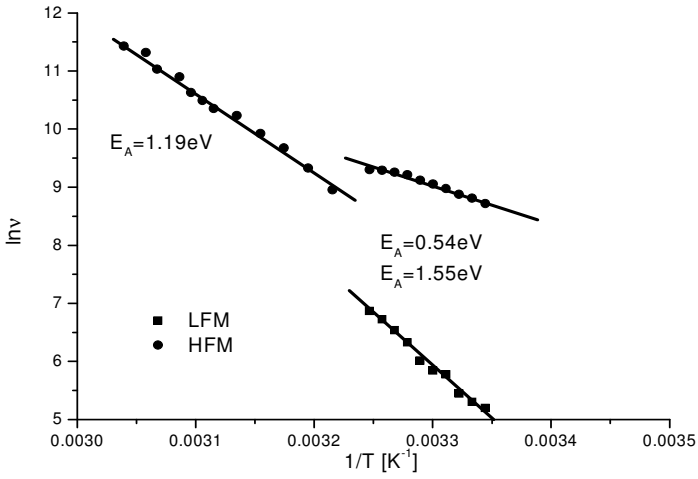


Fig. 8. Arrhenius plots for the relaxation processes in the ferrielectric phase of M3No1 mixture [12]

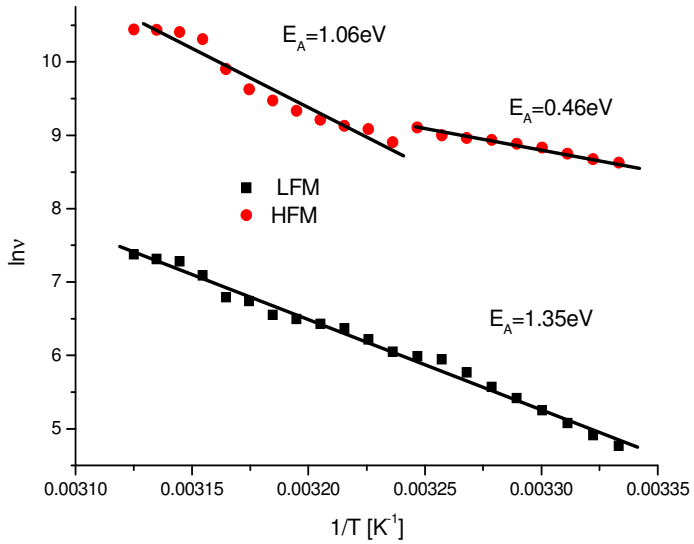


Fig. 9. Arrhenius plots for the relaxation processes in the ferrielectric phase of M3No2 mixture

3.4. Dielectric strength of relaxation modes

The results of dielectric strengths for all investigated mixtures are shown in Fig. 10. The dielectric strengths of M1 mixture are $\Delta\varepsilon = 1$ for HFM and change from $\Delta\varepsilon = 1$ to $\Delta\varepsilon = 0.5$ with growing temperature for LFM.

In the M3No1 mixture the dielectric strength of LFM modeis rather constant in this temperature range and equal to about $\Delta\varepsilon = 4$ to above 35°C. Then grows to maximum $\Delta\varepsilon = 9$ at about 38°C and rapidly goes down with grows temperature.The dielectric strength of LFM modeincreases with increasing temperature. The dielectric strength changes from $\Delta\varepsilon = 1$ at 25°C up to about $\Delta\varepsilon = 2.2$ at 32°C.

In the M3No2 mixture the dielectric strength of LFM is rather constant to above $\Delta\varepsilon = 1$ with a weak decrease with growing temperature. The HFM changes from $\Delta\varepsilon = 1$ via maximum $\Delta\varepsilon = 2$ at about 38°C to less than 1 at higher temperatures.

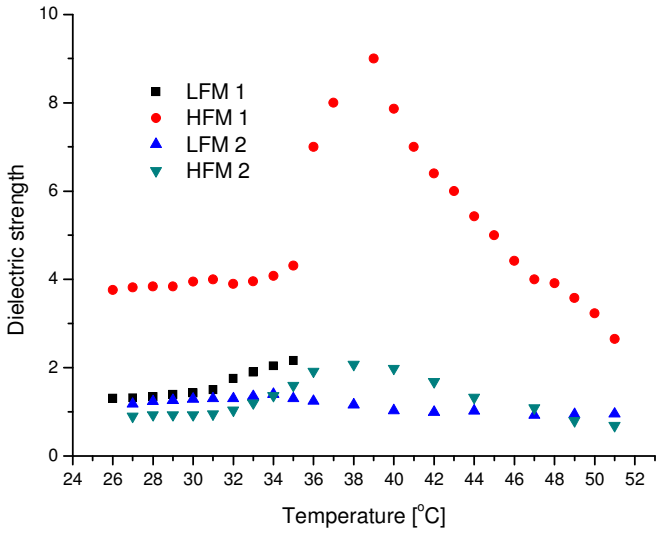


Fig. 10. Temperature dependence of the dielectric strength in theferrielectric phases of M3No1 and M3No2

The temperature dependence of dielectric strength of HFM for both samples of the M3 mixture show a change in characteristics at temperature about 38°C, below this temperature dielectric strength decreases. The Arrhenius plots show different activation energies up to temperature about 35°C and below for both mixtures M3. The activation energy decreases two times below this temperature for both mixtures. It suggests that we have to do with different relaxation processes in these temperature regions.

3.5. The bias field dependence of the dielectric modes

To analyze the relaxation modes in the M3 mixtures DC bias was used. The measurements were made at the lower temperatures where the SLM and ferrielectric GM was detected and are presented in Fig. 12. The results obtained in the higher temperatures (below 38°C) where, together with SLM or without, the HFM dielectric mode exists are presented in Fig. 11.

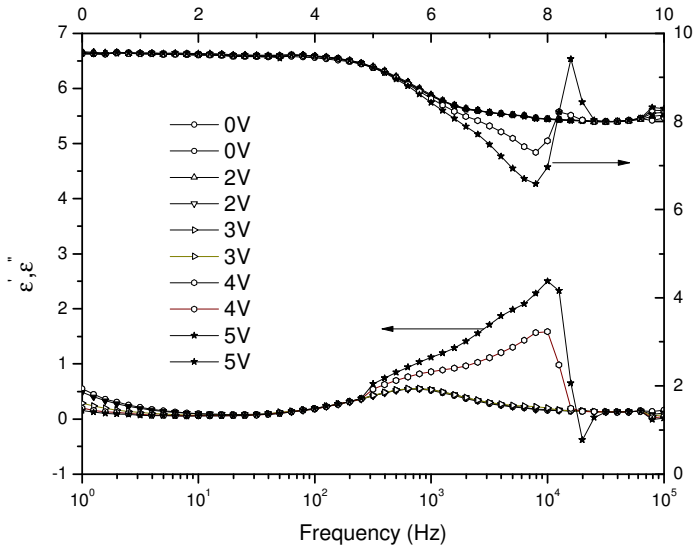


Fig. 11. Dielectric permittivity and dielectric loss as a function of frequency at different biases in 5 μm thick cell at temperature 40°C for the M3No1 mixture

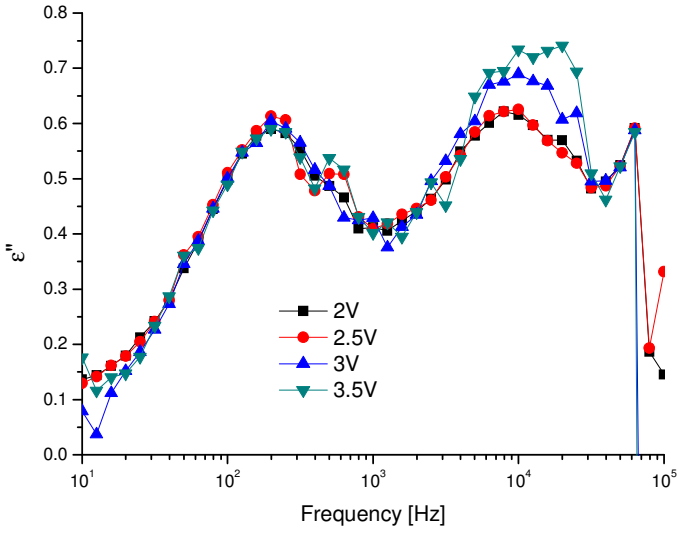


Fig. 12. Dielectric lossas a function of frequency at different biases in 5 μm thick cell at temperature 30°C for the M3No2 mixture

No influence of DC bias on SLM (LFM) was detected for M3 mixtures.

No influence of the biasing voltage on HFM mode has been registered up to 2V/5 μm, but a rapid increase of dielectric strength in the range 2V/5 μm to 5V/5 μm has been detected for M3No1 mixture in the higher temperature range. The changes of dielectric response by the DC bias shown in Fig. 11 and are difficult to comment. In the lower temperature range of HFM (example for M3No2 mixture at 30°C presented in Fig. 12) one can see the grow of amplitude of dielectric loss wit DC bias. These result of influence DC bias of observed dielectric modes do not shed more light on the interpretation ofits nature in our case.

Growing of the amplitude of dielectric relaxation mode is registered for soft mode [16] and for the ferrielectric GM [8] for low DC bias.The growing of amplitude of dielectric mode with DC bias in lower temperatures of all mixtures, confirms that in this temperature range ferrielectric GM exist. The nature of the mode in higher temperatures is rather speculative and it could be soft mode or the mode related to $\mathrm{Sm}C^*_\beta$ [17] phase or subphase mixture.

4. CONCLUSIONS

1. In the ferrielectric $\mathrm{Sm}C^*_\gamma$ phase two relaxation modes were observed in the M1 mixture and M3 mixtures.
2. The lower frequency mode did not change with DC bias and was interpreted as the surface layer mode for all mixtures.
3. The high relaxation mode is inhomogeneous and at higher temperatures changes his nature. In lower temperature range ofthe ferrielectric phase it is ferrielectric GM, but at higher temperatures it could be the soft mode or the mode related to $\mathrm{Sm}C^*_\beta$ phase or phase mixture.

REFERENCES

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

[2] **Musevic I., Blinc R., Zeks B.,** *The Physics of ferroelectric and antiferroelectric Liquid crystals*, World Scientific Publishing Co. Pte. Ltd., Singapore 2000, pp. 478-480.

[3] **Górecka E., Pociecha D., Cepic M., Zeks B., Dąbrowski R.,** Phys. Rev. E, **65** (2002) 061703.

[4] **Buivydas M., Gouda F., Andersson G., Lagerwall S.T., Stebler B., Bomelburg J., Heppke G., Gestblom B.,** Liq. Crystals, **23** (1997)723.
[5] **Bourny V., Pavel J., Gisse P., Nguyen H.T.,** Ferroelectrics, **241** (2000)247.
[6] **Sarmento S., Simeao Carvalho P., Chaves M.R., Pinto F.,** Liquid Cryst., **28** (2001) 673.
[7] **Pandey M.B., Dhar R., Dąbrowski R.,** *Ferroelectrics,* **343** (2006) 83.
[8] **Kundu S.K., Aoki Y., B.K. Chaudhuri B.K.,** Liquid Crystals **31** (2004) 787.
[9] **Ghosh S., Nayek P., Roy Kr., Majumder T.P., Dąbrowski R.,** Liq. Cryst. **37** (2010) 369.
[10] **Wojciechowski M., Bąk G.W., Tykarska M.,** Opto-electronic Rev. **16** (2008) 257.
[11] **Wojciechowski M.,** Sci. Bull. Tech. Univ. Lodz. No.1010, Phys., **28** (2007) 105.
[12] **Wojciechowski M.,** Sci. Bull. Tech. Univ. Lodz. No.1057, Phys., **30** (2009) 85.
[13] **Skrzypek K., Tykarska M.,** Ferroelectrics, **343** (2006) 177.
[14] **Hiller S., Biradar A.M., Wróbel S., Haase W.,** Phys. Rev. E. **53** (1996) 641.
[15] **Ahuja J.K., Raina K.K.,** Japan. J. Appl. Phys. **39** (2000) 4076.
[16] **Marcerou J.P., Nguyen H.T., Bitri N., Gharbi A., Essid S., Soltani T.,** Eur. Phys. J. E **23** (2007) 319.
[17] **Lagerwall J., Giesselmann F., Rauch S., Heppke G., Rudquist P., Lagerwall S.,** Ferroelectrics, **315** (2005) 221.

DIELEKTRYCZNE WŁASNOŚCI FAZY FERRIELEKTRYCZNEJ INDUKOWANEJ W MIESZANINIE CIEKŁYCH KRYSZTAŁÓW

Streszczenie

W pracy przedstawiono i porównano dielektryczne charakterystyki fazy ferrielektrycznej zarejestrowanej w dwóch składach mieszaniny, otrzymane w komórkach o złotych elektrodach i uporządkowaniu planarnym. W fazie ferrielektrycznej badanych mieszanin zarejestrowano dwa procesy relaksacyjne. W obszarze dziesiątków kHz ferrielektrycznym od Goldstone'a występuje w całym obszarze fazy ferrielektrycznej. Nie jest on jednorodny w całym przedziale temperatur, w wyższych temperaturach ma inną energię aktywacji i temperaturową zależność inkrementu dielektrycznego. Może to być softmod lub inny rodzaj fazy ferrielektrycznej. Drugi proces relaksacyjny w obszarze częstości 0.2-0.8 kHz związany z widocznymi liniami dysklinacyjnymi na powierzchni ciekłego kryształu, tzw. SLM, może występować w części niskotemperaturowej fazy ferrielektrycznej bądź w całym przedziale temperatur tej fazy.