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DIELECTRIC PROPERTIES OF FERRIELECTRIC SUBPHASE OF LIQUID CRYSTAL MHPOPB

The antiferroelectric liquid crystal with relatively broad temperature range of ferrielectric subphase was chosen for dielectric investigations of this subphase. In the ferrielectric subphase, collective molecular motions were registered as a ferrielectric Goldstone mode. Theory of ferroelectric Goldstone mode was applied to the registered ferrielectric subphase to obtain rotational viscosity.

Keywords: dielectric relaxations, ferrielectric Goldstone mode.

1. INTRODUCTION

Antiferroelectric liquid crystals show not only antiferroelectric and ferroelectric phases, but frequently also the smectic chiral subphases. In the cooling process the following phases and subphases may appear: Iso→SmA*→SmC*→SmC$^*_\alpha$→SmC$^*_\beta$→SmC$^*_\gamma$→SmC$^*_A$→Cr [1]. The subphases exist typically in a rather narrow temperature range as for standard antiferroelectric liquid crystalline material MHPOBC [2].

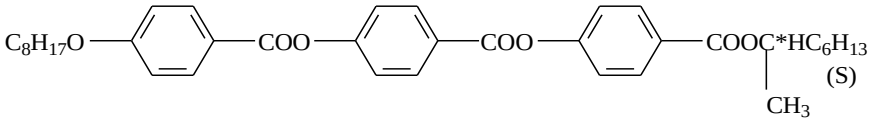
The temperature ranges of various subphases in MHPOPB proves to be substantially broader but it was not clear what phases and subphases does occur in this material. Kuczyński *et al*. [3] suggested that three various chiral smectic subphases occur in MHPOPB. Our earlier investigations [4] supported the suggestions by Kuczyński *et al*. The MHPOPB was investigated dielectrically in our earlier work [4].

The investigations were carried out in the cells with ITO electrodes. The results confirm existence of three subphases (SmC^*_α, SmC^*_β, SmC^*_γ) in this compound and especially broad range of ferrielectric SmC^*_γ phase.

In this work, the new dielectric investigations of MHPOPB were performed. For the presented investigations we used gold electrodes in order to avoid the influence of ITO electrodes on the dielectric response and to obtain more precise results. The present investigations are focused on dielectric characteristic of ferrielectric SmC^*_γ subphase. Theory of ferroelectric Goldstone mode has been applied for the observed ferrielectric subphase. The rotational viscosity has also been calculated from the results.

2. EXPERIMENTAL

Antiferroelectric liquid crystalline compound MHPOPB presented below, with relatively broad temperature range of ferrielectric subphase, has been investigated dielectrically:



The investigated compound was synthesized in the Institute of Chemistry, Military University of Technology (Warsaw) [5].

The phase sequence in the investigated compound has been reported to be as follows :

Cr87.8℃→SmC_A*60.5℃→SmC_γ 89.8℃→SmC_α 94,5℃SmA→141.2℃Iso [5]
Iso 142℃→SmA^* 96℃→C^*_α 89℃→C^*_β 83℃→ C^*_γ 62℃→Hex. [3]
SmA^* 96℃→C^*_α 89℃→C^*_β 62℃→ C^*_γ 49.5℃→Cr [4]
SmA^* 97℃→C^*_α 88.5℃→C^*_β 70℃→ C^*_γ 49℃ →Cr [present investigations]

The dielectric measurements were performed for the liquid crystal compound placed between two parallel glass plates with 5×5 mm gold electrodes. We used standard cells, commercially available from AWAT. The used cells give planar orientation. The sample thickness was d = 5 μm. The measuring sinusoidal signal (0.1 V) was applied nearly perpendicularly to the director of smectic layers. The measurements were carried out with Solartron 1260 A 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.

3. RESULTS AND DISCUSION

The temperature dependencies of the real part of dielectric permittivity at constant frequencies are shown in Fig. 1 for the MHPOPB compound. This temperature dependence reflects phase sequence upon cooling. Similar temperature dependence of the dielectric permittivity were obtained previously [4]. The phase transition from isotropic phase to chiral smectic subpphase SmC^*_α has been detected. The structure of this subphase is still discussed. The next subphase registered in the material is antiferroelectric SmC^*_β subphase [6].

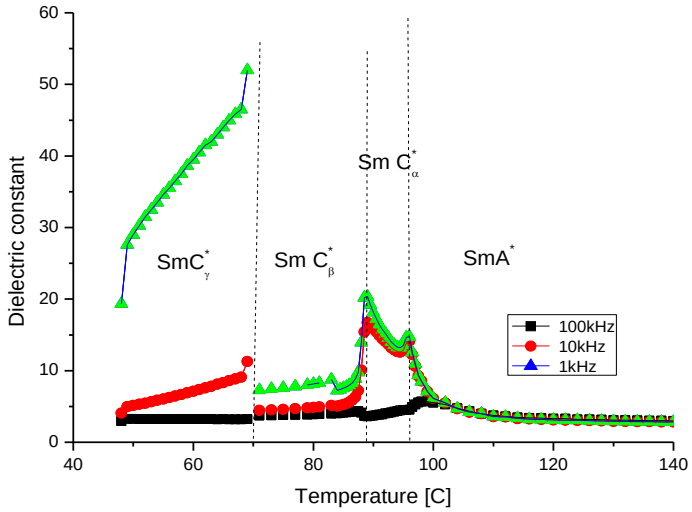


Fig. 1. Real part of dielectric permittivity vs. temperature for the whole temperature range investigated at chosen frequencies

In further cooling, the ferrielectric SmC_{γ}^{*} subphase appears. Only one relaxation mode was detected in each subphase.

The Havriliak-Negami equation was used for fitting the experimental data. Both the dielectric strength and the relaxation frequency of all registered relaxation processes are shown in Fig. 2.

In the SmC_{α}^{*} phase, some kind of phason is suggested to occur, its amplitude increases with increasing external dc field as it results from our earlier results [4]. The relaxation mode observed in the SmC_{β}^{*} phase, which has the antiferroelectric nature, was interpreted as azimuthal in anti-phase reorientation of the director with constant tilt. The ferrielectric Goldstone-like mode detected previously in the SmC_{γ}^{*} phase shows Arrhenius-like temperature dependence. The amplitude of this mode decreases with increasing dc bias like in the case of the typical ferroelectric Goldstone mode.

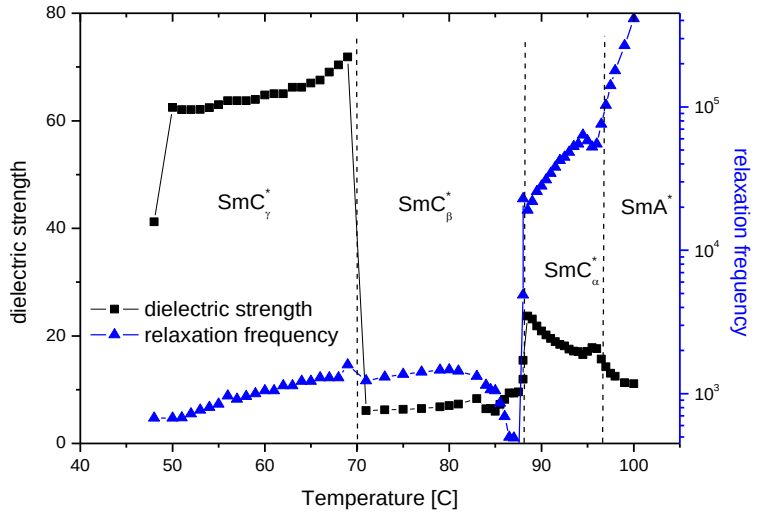


Fig. 2. Temperature dependence of dielectric strength and relaxation frequency of dielectric modes registered in MHPOPB

Theoretical description of Goldstone mode of ferroelectric phase is well known [7,8]. The theoretical formulae describing relaxation frequency and dielectric strength were used for classical ferroelectric Goldstone mode to determine Goldstone rotational viscosity [9-14].

In the ferroelectric phases, as predicted by generalized Landau model, the dielectric strength and the relaxation frequency of the Goldstone mode can be written as [7,8]:

$$\Delta\varepsilon_G = \frac{1}{2\varepsilon_0 K_{33} q^2}\left(\frac{P_S}{\theta}\right)^2$$

$$f_G = \frac{K_{33} q^2}{2\pi\gamma_G}$$

where K_{33}, γ_G, P_S, and θ are the elastic constant, the coefficient of rotational viscosity, the spontaneous polarization, and tilt angle respectively, $q = 2\pi/p$ is the helical wave vector of helical pitch p. From these equations the rotational viscosity γ_G constant could be calculated:

$$\gamma_G = \frac{1}{4\pi\varepsilon_0 \Delta\varepsilon_G f_G}\left(\frac{P_S}{\theta}\right)^2$$

The above formula was used to calculate the rotational viscosity related to ferrielectric-like Goldstone mode. The values of P_S and θ were taken from the work [3]. In the SmC_γ^* subphase, the unit cell consists of three layers but the polarisation of two of them is compensated and only every third layer gives rise to macroscopic polarisation. For this reason, the value of spontaneous polarisation obtained for SmC_γ^* subphase is divided by 3. In paper [15], the experimental results of the spontaneous polarisation in SmC_γ^* are presented. It is suggested that the values of the spontaneous polarisation in ferro- and ferri-subphases should be related as 3:1. The calculations were performed in the temperature range 60°÷70°C. In these temperatures the data necessary to calculate the Goldstone rotational viscosity are available in work [3]. In this temperature the calculated rotational viscosity changes from 113mPas at 60°C to 59mPas at 70°C in the SmC_γ^* phase of MHPOPB. It is risky to compare the calculated values of γ_G with other results for ferroelectric phases, because the value γ_G depends both on spontaneous polarization and dielectric strength, it depends also on temperature. There are a few values of γ_G available: 5÷10 mPas, Kuczyński *et al*. [9], 50÷300mPas, Goswami *et al*. [11], 70÷240 mPas, Hemine *et al*. [12].

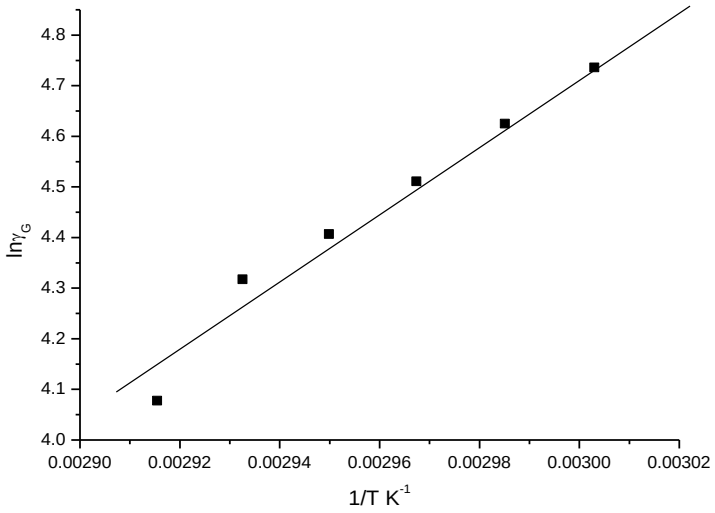


Fig. 3. Arrhenius plot of ferrielectric Goldstone rotational viscosity for MHPOPB. Values of ferrielectric Goldstone mode viscosity are taken in mPas

The Arrhenius law was used to evaluate of the rotational viscosity activation energy in the following formula:

$$\gamma_G = \gamma_0 \exp\left(\frac{E_A}{k \cdot T}\right)$$

where E_A is the activation energy. Plot of $\ln\gamma_G$ versus inverse of temperature is presented in Fig. 3 and shows linear behaviour. The obtained activation energy is equal 0.60 eV for ferrielectric SmC_γ^* subphase of MHPOPB.

The obtained activation energy differs a little from values obtained for ferroelectric phase of other materials: 0.32eV and 0.42eV for two compounds [14], and 0.51 for DOBAMBC [16]. However, the temperature dependence of γ_G in all the papers and in this work remains of Arrhenius type.

Though the calculated values of γ_G for the ferrielectric phase are close the values of γ_G found for ferroelectric phase of other materials, the applicability of generalized Landau model for ferroelectric phase of ferrielectric liquid crystalline materials is an open question.

CONCLUSIONS

1. The investigated MHPOPB antiferroelectric liquid crystal compoud shows ferrielectric SmC_{γ}^{*} subphase in relatively broad temperature range.
2. The dielectric characteristic (*i.e.* the temperature dependence of both dielectric strength and relaxation frequency) in cells with gold electrodes are similar but not identical to those obtained in cells with ITO electrodes.
3. The ferroelectric theory of Goldstone mode was used to determine the ferrielectric Goldstone rotational viscosity. The obtained values of rotational viscosity should be treated as the first approximation, because it is difficult to estimate applicability of the model for ferroelectric subphase.
4. The obtained values of viscosity shows Arrhenius-type temperature dependence with activation energy equal to 0.60eV.

REFERENCES

[1] **Lagerwall J.P.F., Rudquist P., Lagerwall S.T., Gieβelmann F**., Liq. Cryst., **30** (2003) 399.
[2] **Hou J., Schacht J., Giebelmann F., Zugenmaier P.**, Liq. Cryst., **22** (1997) 409.
[3] **Kuczyński W., Goc F., Dardas D., Dąbrowski R., Hoffmann J., Stryła B., Małecki J.,** Ferroelectrics, **274** (2002) 83.
[4] **Wojciechowski M., Gromiec L.A., Bąk G.W.,** J. Mol. Liq., **124** (2006) 7.
[5] **Dąbrowski R., Drzewiński D., Czupryński K., Gauza S., Kenig K., Kuczyński W., Goc F**., Mol. Cryst. and Liq. Cryst., **365** (2001) 199.
[6] **Górecka E., Pociecha D., Cepic M., Zeks B., Dąbrowski R**., Phys. Rev. E, **65** (2002) 061703.
[7] **Carlson T., Zeks B., Levstik A., Filipic C., Levstik I., Blinc R.,** Phys. Rev. A, **42** (1990) 87.
[8] **Singh A., Singh S.,** Liq. Cryst. **35** (2008) 727.
[9] **Kuczyński W., Dardas D., Nowicka K.**, Phase Transitions **82** (2009) 444.
[10] **Kuczyński W., Dardas D., Hoffmann J., Nowicka K., Jeżewski W.**, Phase Transitions, **85** (2012) 358.

[11] **Goswami D., Sinha D., Debnath A., Mandal P.K., Gupta S.K., Haase W., Ziobro D., Dąbrowski R.,** J. Mol. Liquids, **182** (2013) 95.
[12] **Hemine J., Daoudi A., Legrand C., El Kaaouachi A., Zazoui M., Isaert N., Nguyen H.T**., Spectroscopy Letters, **41** (2008) 285.
[13] **Boussousalem Y., Ismaili M., Buisine J.M., Binet C., Joly G., Nguyen H.T.,** Liq. Cryst., **36** (2009) 899.
[14] **Hemine J., Daoudi A., Legrand C., El Kaaouachi A., Nafidi A., Isaert N., Nguyen H.T**., M.J. Cond. Matter, **12** (2010) 225.
[15] **Shytkov N.M., Vij J.K., Barnik M.I., Nguyen H.T.,** Cryst. Reports, **45** (2000) 682.
[16] **Levstik A., Kuntjak Z., Filipic C., Levstik I., Bregar Z., Zeks B., Carlsson T.,** Phys. Rev. A **42** (1990) 2204.

WŁASNOŚCI DIELEKTRYCZNE FAZY FERRIELEKTRYCZNEJ ZWIĄZKU CIEKŁOKRYSTALICZNEGO MHPOPB

Streszczenie

Antyferroelektryczny związek ciekłokrystaliczny MHPOPB posiadający szeroki temperaturowy zakres występowania fazy ferrielektrycznej, poddano badaniom dielektrycznym w komórkach o złotych elektrodach. Otrzymane dielektryczne charakterystyki związku są zbliżone do tych, które otrzymano we wcześniejszej pracy w komórkach z elektrodami ITO. Temperaturowe zależności częstości relaksacji i inkrementu dielektrycznego fazy ferrielektrycznej użyto do obliczenia rotacyjnej lepkości charakteryzującej ferrielektryczny mod Goldstone'a, analogicznie jak dla fazy ferroelektrycznej. Otrzymane wyniki dla fazy ferrielektrycznej są zbliżone do otrzymanych dla fazy ferroelektrycznej innych związków.