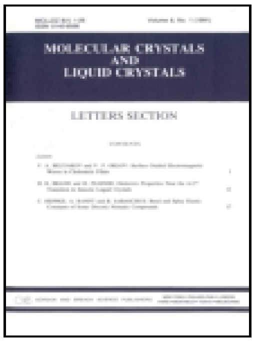

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Molecular and Intramolecular Motions in Dual-Frequency Nematic Liquid Crystal, at Extra Low Temperatures, Observed by Means of Dielectric Spectroscopy

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New dual frequency nematic liquid crystal mixture has been prepared and investigated by means of dielectric spectroscopy in a wide temperature range (from 120°C to −100°C). The molecular structures of compounds used to prepare the final mixture and mixture's composition influence its dielectric properties. Wide temperature investigations show how molecular and intramolecular motions change with temperature. It is possible at low temperatures to slow down intramolecular motions so much that they are visible in dielectric spectroscopy. At −80°C molecular motions disappear from dielectric response. At −100°C all thermally activated motions are too slow to be detected by means of dielectric spectroscopy.

Keywords dual frequency nematic; relaxation frequency; Havriliak-Negami model; molecular modes; S-mode; L-mode; intramolecular modes

Introduction

Dielectric spectroscopy is a powerful experimental technique to characterize dual-frequency nematic liquid crystal (DFNLC) [1–4]. DFNLC in contrast to 'classical' nematic liquid crystal (NLC) has positive ($\Delta\varepsilon_p > 0$) and negative ($\Delta\varepsilon_n < 0$) dielectric anisotropy in a specific frequency range [5–7]. This property allows us to obtain short switching on- and off-times [8–9]. Important parameters from application point of view are: dielectric anisotropy ($\Delta\varepsilon$) and crossover frequency (f_C). At crossover frequency dielectric anisotropy changes its sign [3]. All of mentioned parameters can be assessed by dielectric spectroscopic measurements.

To compare 'classical' NLC and DFNLC, equations for the rise time (on-time τ_{ON}) and decay time (off-time τ_{OFF}) are presented in the Table 1. One can see that for 'classical' nematics on- and off-times depend on cell gap (d), rotational viscosity (γ) and effective

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Table 1. Examples of molecular structures of molecules creating investigated DFNLC

Switching on- and off- times in NLC	Switching on- and off- times in DFNLC
$\tau_{ON} = \frac{\gamma d^2}{\varepsilon_0 \Delta\varepsilon V^2 - \pi^2 k_{eff}}$	$\tau_{ON} = \frac{\gamma d^2}{\varepsilon_0 \Delta\varepsilon_p V^2 - \pi^2 k_{eff}}$
$\tau_{OFF} = \frac{\gamma d^2}{\pi^2 k_{eff}}$	$\tau_{OFF} = \frac{\gamma d^2}{\varepsilon_0 \Delta\varepsilon_n V^2 + \pi^2 k_{eff}}$

elastic constant (k_{eff}). Additionally on-time depends on applying voltage (V) and dielectric anisotropy ($\Delta\varepsilon$). One can see that for ‘classical’ nematics only the on-time can be shortened by applied electric field. Such conditions results in short rise and long decay times in NLC. Situation is different in DFNLC. In both cases switching times strongly depend on applied electric field V and dielectric anisotropies, positive ($\Delta\varepsilon_p$) for τ_{ON} and negative ($\Delta\varepsilon_n$) for τ_{OFF}. Thus one can find in DFNLC nearly the same τ_{ON} and τ_{OFF} times.

To create the dual-frequency nematic liquid crystal we need to mix a Base Mixture (BM) which shows negative dielectric anisotropy and an AdMixture (AM) which shows positive dielectric anisotropy [1–2, 10–11]. Base mixture is composed by molecules with dipole moments perpendicular to the long molecular axis, while admixture contains molecules with dipole moments parallel to the long molecular axis. It was found earlier [1–2] that, the admixture is responsible for molecular motion around short molecular axis (S-mode) in dual-frequency nematic liquid crystals. Furthermore, molecular rotation around long molecular axis (L-mode) strongly depends on the base mixture.

From previous investigations one can know, that crossover frequency (f_C) strongly depends on relaxation frequency of S-mode [1–4]. In examined DFNLC two relaxation frequencies of S-mode can be found due to the composition of AM. We call them: S_L-mode (low relaxation frequency) and S_H-mode (high relaxation frequency). This work shows how composition of AM affects f_C. Wide temperature investigations (to $-100°C$) allow us to observe how cooling gradually slows down all molecular and intramolecular modes. To describe this effect Havriliak – Negami [12] relaxation model should be used.

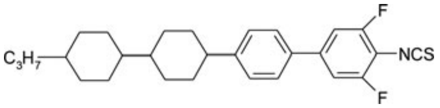
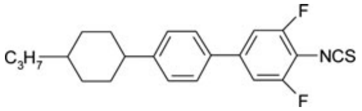
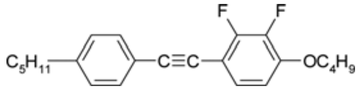
Investigated Material

DFNLC mixture under study was prepared in our laboratory. Such material usually composes of many different molecules [1–4, 10–11]. Three examples of molecular structures can be found in examined DFNLC: A, B and C (Table 2). Molecules of types A and B have longitudinal dipole moments ($\mu_{\|}$), while molecules of type C possess transverse dipole moments ($\mu_{\perp}$). Molecules of types A and B constitute admixture. Type C is an example of molecule, which can be found in base mixture structure. Molecules of type A are more in AM (70% of weight) than type B (30% of weight). What is more, molecular mass of A-molecules are higher than B-molecules.

Experiment

To perform dielectric spectroscopy measurements impedance analyzer HP4192A was used. The impedance analyzer with temperature controller Linkam TMS 93 and THMS-600 heating stage was programmed by Agilent Vee in our lab. It allows obtaining precisely

Table 2. Examples of molecular structures molecules creating investigated DFNLC

Type	Examples of molecular structures
A	
B	
C	

results in a wide frequency and temperature range. DFNLC was investigated by HP4192A in 100 Hz – 10 MHz frequency range. Temperature range was from +120°C to −100°C. To cool samples below room temperature we used dry ice and liquid nitrogen. Experiment was done in a cooling cycle with rate 0.3°C/min. The measurements were taken at every 0.5°C. The dual-frequency nematic liquid crystal was filled to cells by the capillary action in an isotropic phase. The cells with gold electrodes, to reduce their resistivity, were custom made in our laboratory. Two kinds of cells with homogeneous (HG) and homeotropic (HT) alignment were used respectively to obtain electric permittivity in directions perpendicular ($\varepsilon_\perp$) and parallel ($\varepsilon_\parallel$) to the director **n**. Cell gap was around 5 μm. The wires should be as short as is possible to reduce the inductance effect [13–15]. The amplitude of applied voltage was 100 mV to avoid non-linear effect.

Experimental Results

In Fig. 1 the real part (ε') of electric permittivity as a function of temperature (T) for investigated DFNLC is presented. One can see a wide (over 195°C), stable nematic phase. Phase transition from an isotropic phase to the nematic phase is at 95°C. Crystallization temperature is below −100°C. At −100°C we cannot see any dispersion. Thus, all molecular and intramolecular motions are hindered. Dispersion at higher temperatures comes from S-mode and L-mode. S-mode is visible by dielectric spectroscopy in HT cell from 95°C to −15°C. In contrast, L-mode can be observed in both (HG and HT) cells from −10°C to −60°C. Thank to a wide temperature measurements for examined DFNLC one is able to observe temperature dependence of crossover frequencies (Fig. 2). At $f_{\mathrm{Cp-n}}$ dielectric anisotropy [3–4] changes its value from positive to negative one. On the contrary, at $f_{\mathrm{Cn-p}}$ dielectric anisotropy [3–4] changes its sign from negative and positive. At temperature range from 90° to −10°C dielectric anisotropy is positive at low, and negative at high frequency region. The situation is reversed at lower temperatures: from −20°C to −65°C. For instance at temperature 20°C and for frequency 1 kHz $\Delta\varepsilon = 1.85$, while for 100 kHz $\Delta\varepsilon = -2.36$. The biggest disadvantage (from application point of view) of dual-frequency nematic liquid crystals is that f_{C} changes with temperature.

In Figures 3a and 4a one can observe only one relaxation at −50°C at the same frequency domain. This relaxation comes from rotation around long molecular axis (L-mode).

In absorption spectrum (Figure 4b) one can notice the high asymmetry of frequency distribution at low temperatures. Asymmetry distribution comes from intramolecular modes. Thermally activated intramolecular modes, are typically visible in THz range (IR spectroscopy), but low temperature investigations shift the frequency domain for them, as was found for molecular motions earlier [1–2]. At −50°C they can be observed in kHz frequency range by dielectric spectroscopy.

It is worth to notice, that in HT cell two relaxation frequencies of S-mode are observed (Fig. 3b, 4b). The first one is in low frequency region (S_L-mode) and the second one is in high frequency region (S_H-mode). At 30°C relaxation frequency of S_L-mode is around 16.3 kHz while for S_H-mode is around 152 kHz. Both modes are well fit using Cole-Cole model [16] with the distribution parameter α close to zero: 0.0065 and 0.041 respectively. It means that both S_L and S_H -modes in this temperature range are almost Debye-like [17].

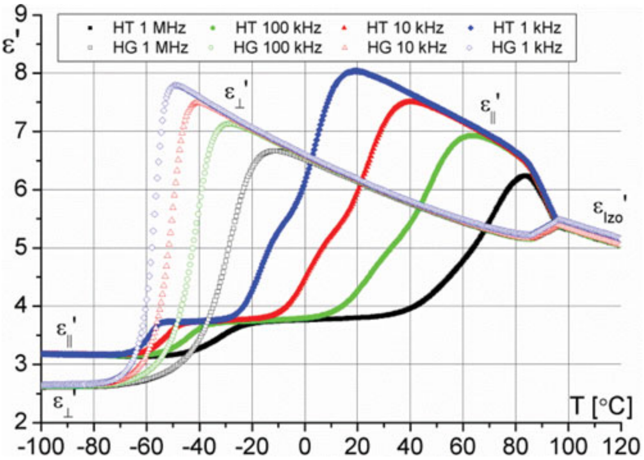


Figure 1. Real part of electric permittivity (ε') measured in HG and HT cells for frequencies: 1 kHz. 10 kHz, 100 kHz, 1 MHz.

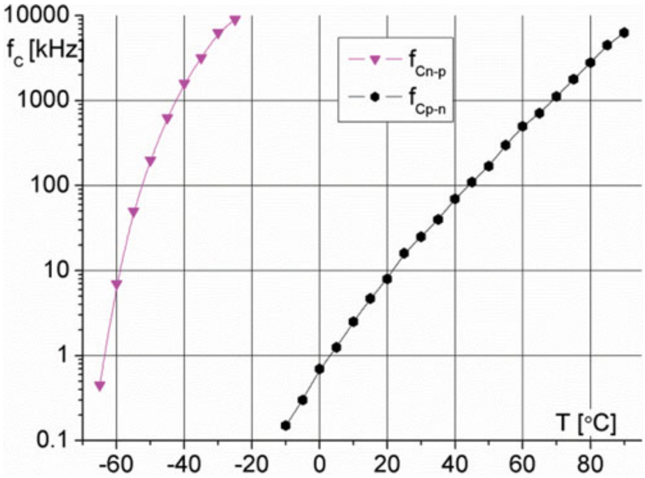


Figure 2. Two kinds of crossover frequencies ($f_{Cp\text{-}n}$ and $f_{Cn\text{-}p}$) upon temperature (T).

In HG cell at 30°C (Fig. 3b) no dispersion is observed.

Results of Calculations

To know the individual character of detected modes, relaxation frequency (f_R) and dielectric strength ($\delta\varepsilon$) were calculated by optimisation procedure presented earlier [4, 12]. For calculation Havrilak-Negami model of relaxation was used. This model can manage with asymmetry of dispersion spectrum, which Cole-Cole model [16] cannot describe. The Havrilak-Negami model: $\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\delta\varepsilon}{[1+(j2\pi f\tau_R)^{1-\alpha}]^\beta}$, where ε_∞ is high frequency limit of electric permittivity, $\delta\varepsilon$ is the strength of mode, τ_R is relaxation time, α is distribution parameter describing the broadness of the relaxation time distribution, while β is the distribution parameter describing the asymmetry of the relaxation time distribution [12].

In Figure 5 relaxation frequencies for L-mode found in our calculations are presented. Relaxation frequencies decrease with temperature decreasing. Difference of f_R in HG and HT cells comes from imperfect alignment and small temperature shift between measuring cells.

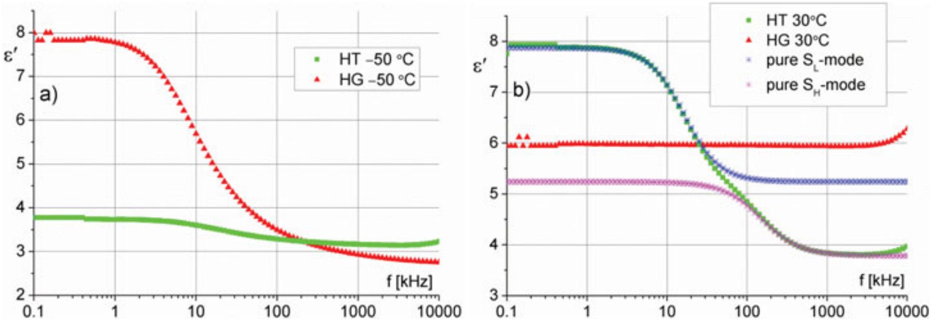


Figure 3. Real part of electric permittivity (ε') versus frequency at a) −50°C and b) 30°C, measured in HG and HT cells. Additionally dielectric response obtained in HT cell at 30°C is analysed as the superposition of two pure modes (S_L and S_H), which can be described by Cole-Cole model.

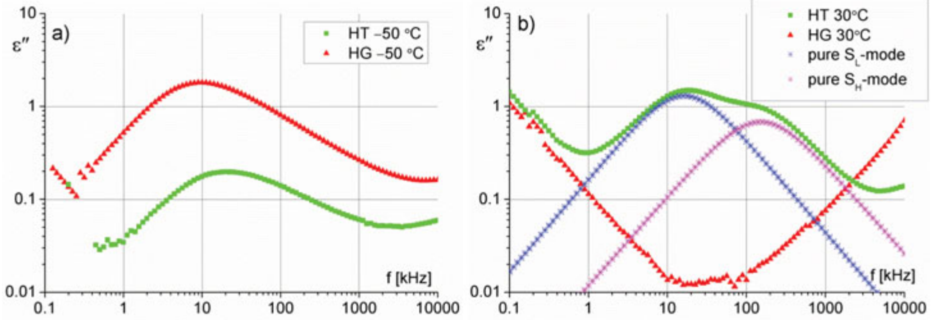


Figure 4. Imaginary part of electric permittivity (ε'') versus frequency at a) −50°C and b) 30°C measured in HG and HT cells. Additionally dielectric response obtained in HT cell at 30°C is analysed as the superposition of two pure modes (S_L and S_H), which can be described by Cole-Cole model.

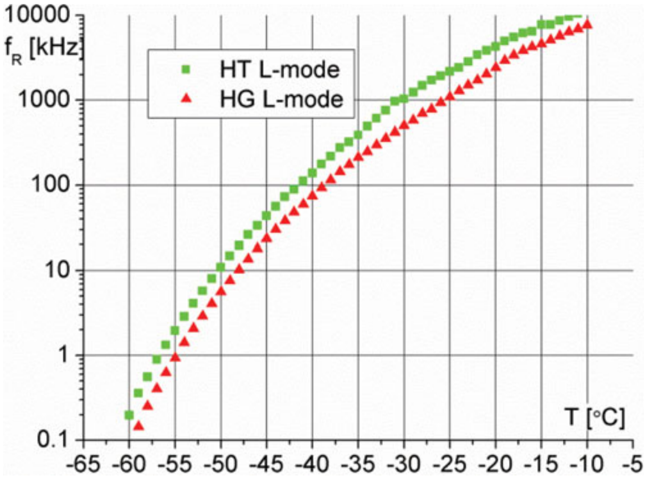


Figure 5. Relaxation frequencies (f_R) calculated for L-mode in HG and HT cells.

In Figure 6 relaxation frequencies of S_L-mode and S_H-mode and crossover frequency as a function of temperature are presented. Crossover frequency $f_{Cp\text{-}n}$ is similar to relaxation frequency of S_L-mode. Discrepancy between relaxation frequencies of S_L- and S_H-modes is constant versus temperature. S_L-mode comes from molecules type A. A-molecules have larger moment of inertia and molecular mass than B-molecules. Therefore relaxation frequency of these molecules should be lower. Molecules of type B are responsible for S_H-mode.

Dielectric strength of all detected modes grows with decreasing temperature (Fig. 7). Magnitude of L-mode is higher in HG cell than in HT one (Fig. 7a). Rotation around long molecular axis appears in HT cell due to imperfect homeotropic alignment. Thus $\delta\varepsilon$ of L-mode measured in HT cell is relatively low. Results from HT cell give higher uncertainty

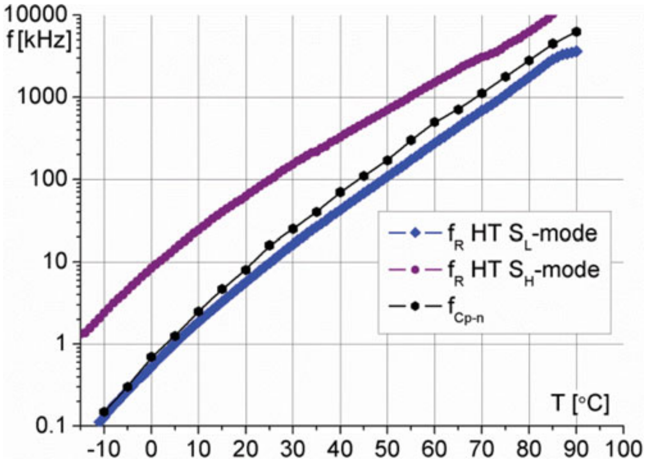


Figure 6. Relaxation frequencies (f_R) of S_L- and S_H-modes and crossover frequency ($f_{Cp\text{-}n}$) versus temperature.

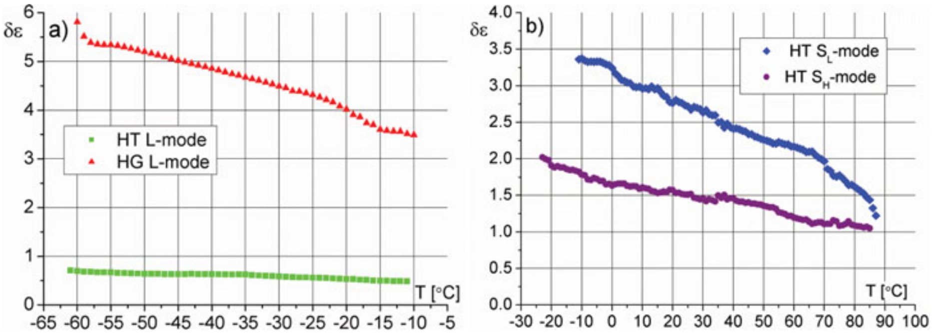


Figure 7. Dielectric strength ($\delta\varepsilon$) for: a) L-mode detected in HG and HT cells and b) S_L and S_H -modes detected in HT cell.

of calculations than results from HG cell. Dielectric strength of S_L-mode in final mixture is higher than dielectric strength of S_H-mode because, there are A-molecules much more than B-molecules in AM.

Intramolecular modes are visible in dielectric spectroscopy when we cool the sample. For the description of this phenomenon Havrilak-Negami model should be used. If we did not observe intramolecular modes in experiment the results would be well described using Cole-Cole model. One can see that Cole-Cole model results are not fitted to experimental ones (Fig. 8a and 8b). At −50°C intramolecular motions are detected in frequency range from 10 kHz to 1 MHz. Asymmetric arc results of many of intramolecular modes. In complicated molecules of liquid crystal one can find dozens of intramolecular vibration and rotations. However by dielectric spectroscopy we cannot distinguish a specific type of vibrations (what is possible in IR spectroscopy) due to the fact that the picture of intramolecular motions obtained in dielectric spectroscopy is averaged.

From Fig. 9 one can deduce that intramolecular modes can be found in dielectric spectroscopy measurements at around −17°C. At this temperature distribution parameter β start dropping down. Asymmetry of frequency distribution is becoming more and more evident. The lower β – the larger intramolecular modes contribution to the dielectric response. Parameter α of distribution for L-mode is low and rather constant (around 0.05)

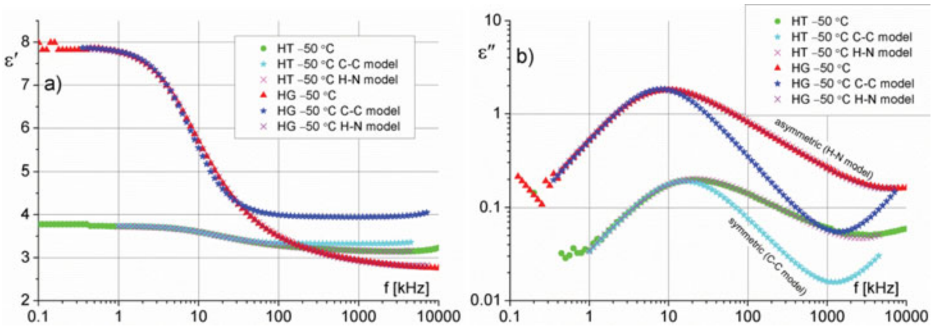


Figure 8. The results of fitting procedure of a) ε' and b) ε'' for L-mode at −50°C in HG and HT cells. When Cole-Cole symmetric model is used fitting procedure does not fit the experimental results for higher frequencies. Asymmetric Havrilak-Negami model can fit the experimental results properly.

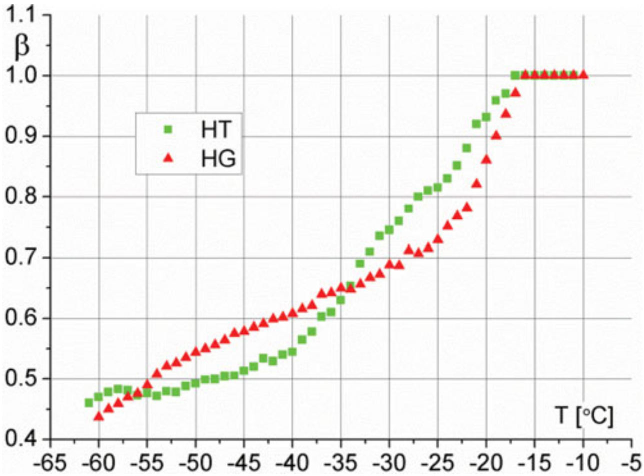


Figure 9. Distribution parameter (β) describing the asymmetry of relaxation times distribution calculated for L-mode in Havrilak-Negami model upon temperature (T) in HG and HT cells.

in for low temperatures. It suggests that L-mode can be described as almost Debye-like mode.

Conclusions

In DFNLC material only one relaxation of S-mode should be observed. Two kinds of S-relaxations can result in dielectric heating effect [18]. Switching of examined dual-frequency liquid crystal by frequency of electric field above crossover frequency may causes induction of maximum of electric losses. To avoid this problem dual-frequency material with the same f_C (crossover frequency) and f_R (relaxation frequency of S-mode) should be applied. Two different types of molecules used in AM results in two relaxation times.

At cooling samples below −100°C all thermally activated modes (molecular and intramolecular) at such low temperature disappear from measuring range of dielectric spectroscopy. No dispersion is observed (Fig. 1). Typical frequencies of intramolecular motions changes from 1 THz (room temperature) to 0.1 kHz (at −100°C) – 10 decades!

At such low temperature only electron polarizability is observed and still responsive to the electric field. Due to the fact that electron polarizability is responsible for refractive index, one can estimate ordinary (n_o) and extraordinary (n_e) refractive indices from dielectric spectroscopy measurement and calculate birefringence Δn of liquid crystal. If we read from Figure 1 electric permittivities ($\varepsilon_\perp$ and $\varepsilon_\parallel$) for temperature −100°C, we can calculate refractive indices and birefringence:

$$n_e = \sqrt{\varepsilon_{||}} = \sqrt{3.20} = 1.79;\ n_o = \sqrt{\varepsilon_\perp} = \sqrt{2.60} = 1.61;$$

$$\Delta_n = n_e - n_o = 1.79 - 1.61 = 0.18.$$

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References

[1] Mrukiewicz, M., Perkowski, P., Garbat, K., Dąbrowski, R. & Parka, J. (2013). *Acta Physica Polonica A*, *124*(6), 940.

[2] Mrukiewicz, M., Perkowski, P., Garbat, K. & Dąbrowski, R. (2014). *Liquid Crystals*, doi: 10.1080/02678292.2014.932451.

[3] Perkowski, P., Mrukiewicz, M., Garbat, K., Laska, M., Chodorow, U., Piecek, W., Dąbrowski, R. & Parka, J. (2012). *Liquid Crystals*, *39*(10), 1237.

[4] Perkowski, P., Mrukiewicz, M., Laska, M., Garbat, K., Piecek, W. & Dąbrowski, R. (2013). *Phase Transitions*, *86*(2–3), 113.

[5] Schadt, M. (1982). *Applied Physics Letters*, *41*(8), 697.

[6] Schadt, M. (1982). *Molecular Crystals and Liquid Crystals*, *89*(1-4), 77.

[7] Xianyu, H. Q., Wu, S. T. & Lin, C. L. (2009). *Liquid Crystals*, *36*(6-7), 717.

[8] Xianyu, H. Q., Gauza, S. & Wu, S. T. (2008). *Liquid Crystals*, *35*(12), 1409.

[9] Lin, X. W., Hu, W., Hu, X. K., Liang, X., Chen, Y., Cui, H. Q., Zhu, G., Li, J. N., Chigrinov, V. & Lu, Y. Q. (2012). *Optics Letters*, *37*(17), 3627.

[10] Dąbrowski, R., Dziaduszek, J., Garbat, K., Filipowicz, M., Urban, S., Gauza, S. & Sasnouski, G. (2010). *Liquid Crystals*, *37*(12), 1529

[11] Dziaduszek, J., Kula, P., Dąbrowski, R., Drzewiński, W., Garbat. K., Urban, S. & Gauza, S. (2012). *Liquid Crystals*, *39*(2), 239

[12] Havriliak, S. & Negami, S. (1967). *Polymer*, *8*(4), 161.

[13] Perkowski, P., Łada, D., Ogrodnik, K., Rutkowska, J., Piecek, W. & Raszewski, Z. (2008). *Opto-Electronics Review*, *16*(3), 271.

[14] Perkowski, P. (2009). *Opto-Electronics Review*, *17*(2), 180.

[15] Perkowski, P. (2012). *Opto-Electronics Review 20*(1), 79.

[16] Cole, K. S. & Cole, R. H. (1941). *Journal of Chemical Physics*, *9*, 341.

[17] Debye, P. (1913). *Ver. Deut. Phys. Gesell. 15*, 777.

[18] Wen, C. H. & Wu, S. T. (2005). *Applied Physics Letters 86*(23), 231104.