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DIELECTRIC PROPERTIES OF FERROELECTRIC LIQUID CRYSTALLINE MATERIAL WITH CHIRAL NEMATIC PHASE

The ferroelectric liquid crystal with nematic N phase has been investigated using broadband low frequency dielectric spectroscopy. The dielectric relaxation modes related to a ferroelectric Goldstone mode were detected only in a narrow temperature range. Well defined relaxation process was detected in the SmB* phase at about 90 Hz.*

Keywords: dielectric relaxations, ferroelectrics, Goldstone mode.

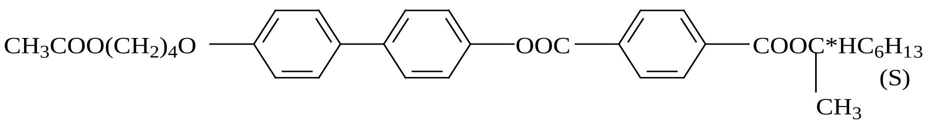
1. INTRODUCTION

Many recently synthetized ferroelectric and antiferroelectric liquid crystals show a lot of phases and subphases. The most often observed phase sequence is as follows: Iso→SmA*→SmC*→SmC$^*_\alpha$→SmC$^*_\beta$→SmC$^*_\gamma$→SmC$^*_A$→Cr [1]. Using the broadband dielectric spectroscopy it is possible to investigate molecular excitations and collective molecular excitation by registrations of relaxation processes corresponding to consecutive types of excitations. In SmA* phase the soft mode is observed as a collective amplitudon mode [2, 3]. In ferroelectric phase both soft mode and Goldstone mode are observed [4, 5], the second one is related to fluctuation in azimuthal angle of ferroelectric helix. Soft mode occurs near the SmA*-SmC* phase transition and Goldstone mode is registered in the whole temperature range of SmC* phase. The Goldstone mode typically shows rather weak temperature dependence of the dielectric strength and the relaxation frequency [6, 7], but quite strong temperature dependence of the two parameters has also been reported [8-10]. The amplitude of Goldstone mode usually decreases with increasing external electric field [11]. In antiferroelectric phase two modes P_L and P_H are often observed. The modes are suggested to be related to the in-phase and anti-phase azimuthal angle fluctuations of directors of the anti-tilted molecules in successive layers [12, 13]. In the ferrielectic SmC^*_γ phase the Goldstone-like mode is often observed [14, 15]. The dielectric investigations may provide useful information about molecular relaxation processes and could be a very handy method for identification of phases and subphases in ferroelectric and antiferroelectric liquid crystals.

The presented investigations are focused on dielectric examination of ferroelectric phase of a ferroelectric compound possessing rather untypical phase sequence. In this compound the ferroelectric phase and chiral nematic N* phase co-exist. The parameters characterising the dielectric response of the investigated LC compound in the temperature range corresponding to liquid crystalline state are presented.

2. EXPERIMENTAL

The dielectric response of the ferroelectric liquid crystalline compound 1H3R (see molecular structure presented below) has been investigated.



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

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

Kr90,7SmB*100SmC*101,8SmA*105N*108,9Izo

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. Planar alignment was strongly supported by polymer coating of electrodes. The sample thickness was d = 5μm. The measuring sinusoidal signal (0.1 V) 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 during heating 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.

3. RESULTS AND DISCUSION

The temperature dependence of real part of dielectric permittivity of the investigated compound for three different frequencies is shown in Fig. 1. Highly polar LC phase is detected below 102°C. However, it results from the data shown in Fig. 1 that the polarization process corresponds to rather low polarization phenomena, just below 1 kHz.

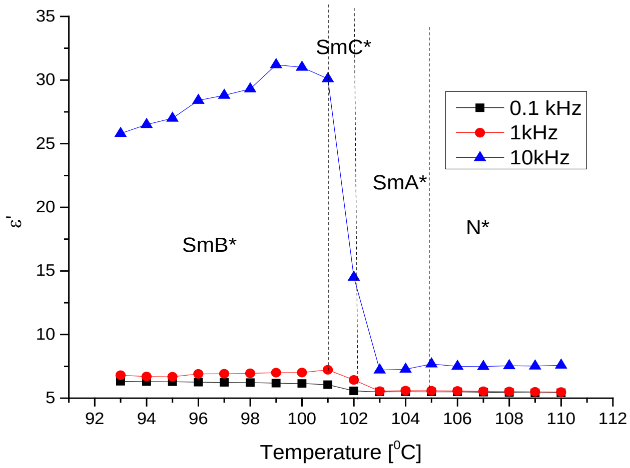


Fig. 1. Real part of dielectric permittivity vs. temperature for the whole temperature range investigated at a few various frequencies

The dielectric responses for different phases are presented in Figs. 2-4. Fig. 2 shows the dielectric response in nematic N* and SmA* phases , no relaxation process in the frequency range is detected. In the SmA* soft mode might probably be registered [4], but the relaxation frequency of this mode is usually in the MHz region, out of our setup possibility.

In Fig. 3 the dielectric response in the SmC* phase is presented. A relaxation process at 101.8°C is noticeable. Clearly defined dielectric relaxations peaks were found only in the temperature range 101.4°C÷101.8°C and are additionally presented in Fig. 4 in the double logarithmic plot. These relaxation peaks may probably be attributed to ferroelectric phase due to correlation between the temperature ranges. The experimental results were fitted with Havriliak-Negami equations. The example of fitting procedure is presented in Fig. 5.

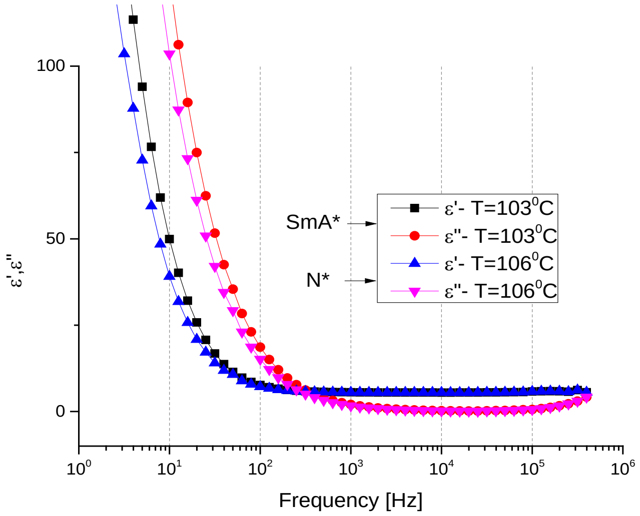


Fig. 2. Dielectric response in the SmA* and nematic N* phases

Taking into account all the data characterizing the relaxations detected in the temperature range 101.4°C÷101.8°C and the coincidence of this temperature range and the range of SmC* phase reported earlier [16] it is justified to suggest that the relaxations shown in Fig. 4 are related to the Goldstone mode due to the phase fluctuations in the azimuthal orientation of the director.

The obtained relaxation peaks parameters are shown in Table 1. The relaxation frequency for the Goldstone mode is of the order of a few kHz typically. In our case the relaxation frequency fluctuate with temperature but all the values are in the kHz region. The dielectric strength changes with temperature too, but the high value of dielectric strength are quite typical for Goldstone mode registered in SmC* ferroelectric phase.

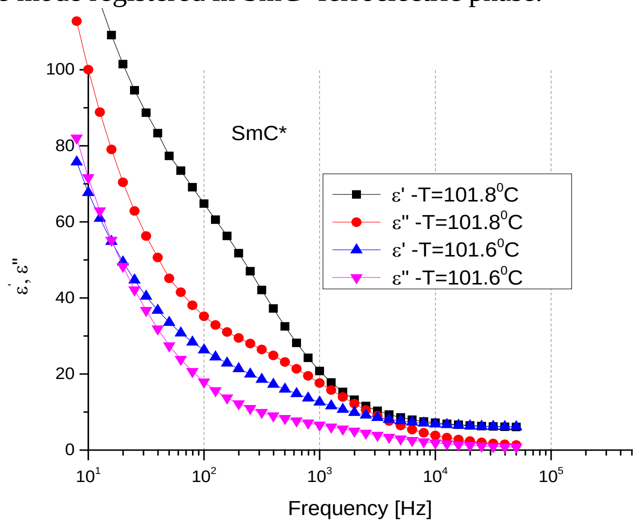


Fig. 3. Dielectric response in the ferroelectric SmC*phase

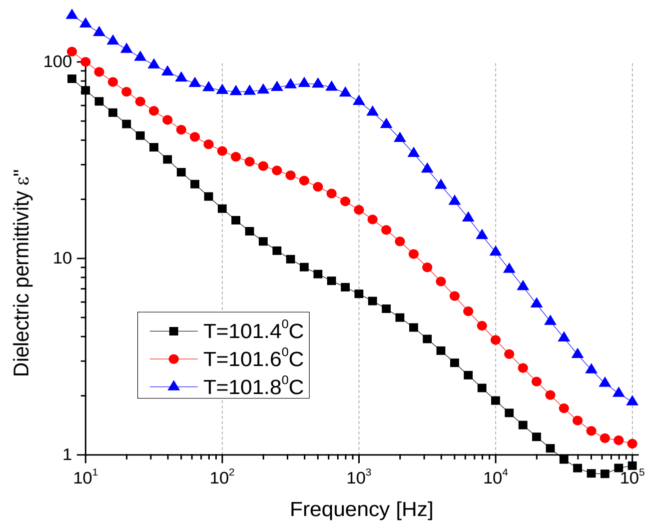


Fig. 4. Imaginary part of dielectric permittivity as a function of frequency for the Goldstone mode for three various temperatures

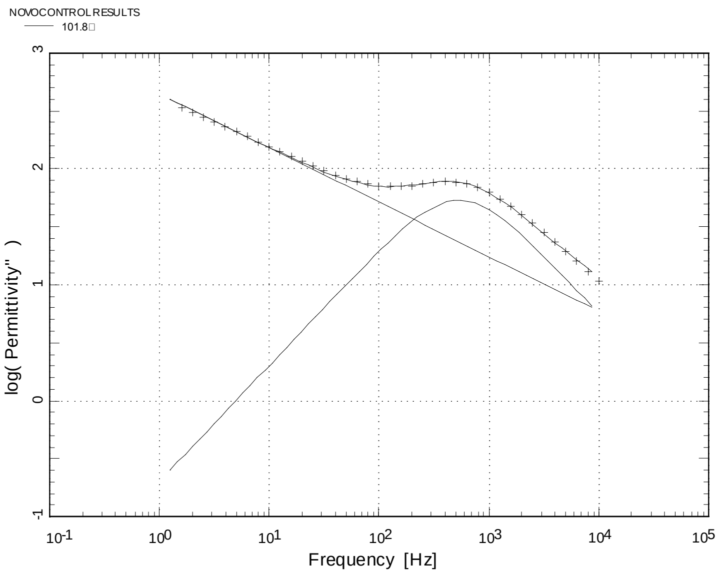


Fig. 5. Example of fitting procedure for the Goldstone mode using Havriliak-Negami equation. The data for T = 101.8^{0}C are presented in the figure

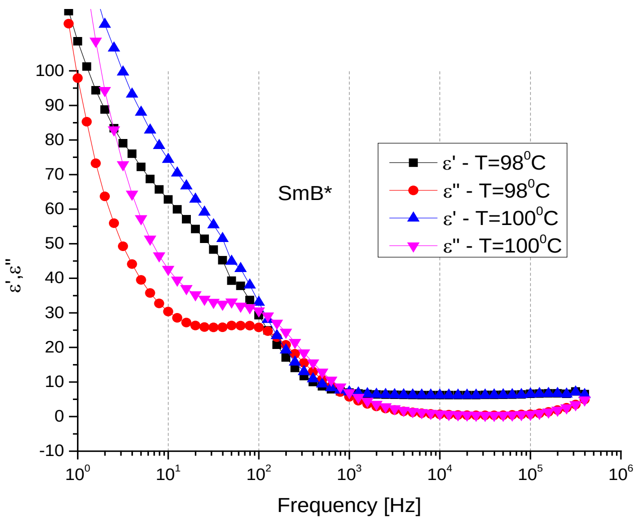


Fig. 6. Dielectric responses in the SmB* phase in two temperatures

Table 1

Parameters of relaxations at 101.4°C ÷101.8°C fitted with HN equation. The MSD parameter shows adjustment to experimental curve

σ[S/cm] 10^{-9}	n	Δε	τ 10^{-4}[s]	ν_R [Hz]	α	β	MSD 10^{-2}	T[^{0}C]
5.2	0.62	67	1.48	1076	0.82	1	3.1	101.4
3.9	0.67	71	3.4	468	0.67	1	3.9	101.6
30	0.56	144	3.57	446	0.90	1	3.6	101.8

In the SmB* phase clearly defined stable peaks appear in the frequency range 60-90 Hz with dielectric strength about Δε = 50. The parameters of this mode are presented in Table 2. The high value of dielectric strength suggests some kind of collective molecular oscillation mode.

Table 2

Parameters of relaxations in the range of SmB* phase

σ[S/cm] 10^{-10}	n	Δε	τ 10^{-3}[s]	ν_R [Hz]	α	β	MSD 10^{-2}	T[^{0}C]
4.9	0.65	47.5	1.9	83	0.98	1	2.1	95
5.3	0.65	48	1.89	82	0.98	1	2.05	96
5.96	0.65	47	1.83	87	0.98	1	2.08	97
6.84	0.65	46.5	1.76	90	0.99	1	2.15	98
9.13	0.65	48.9	1.72	93	0.99	1	2.2	99
11	0.65	49.2	1.77	89	0.99	1	2.4	100
25	0.66	57	2.67	60	0.96	1	4.2	101

Mishra et. al [16] investigated the dielectric properties of a similar compound possessing quite similar phase sequence, but showing much broader temperature range of SmC* phase. They registered Goldstone mode in SmC* phase, some additional relaxation processes in the N* was interpreted as a soft mode and another weak relaxation process in the SmB* phases has also been detected. The relaxation process in the SmB*phase was ascribed to the short-axis relaxation mode (molecular motion around short axis of molecule). Such relaxations round short axis may be expected to be much slower than any other molecular relaxation process so comparatively small values of the relaxation frequency should not be surprising. However, the values of relaxation frequencies registered in our samples are approximately two orders of magnitude smaller than those presented by Mishra et.al. In this situation the interpretation of the relaxation process in SmB* phase in the investigated LC material remains an open problem.

4. CONCLUSIONS

1. The dielectric measurements confirm the existence of the ferroelectric phase in a relatively narrow temperature range between $101.4^0C \div 101.8^oC$ in the investigated compound.
2. The Goldstone mode detected in SmC* phase exhibits a relatively low but reasonable relaxation frequency close to 1 kHz.
3. Low frequency dielectric relaxation mode was detected in the SmB* phase in the frequency range 60-90 Hz, the mode is probably related to some kind of collective molecular motion.
4. No dielectric relaxation modes were detected in the SmA* and nematic N* phases in the frequency range used.
5. 1H3R compound presented in this paper is very similar to 1H6Bi [15] compound, the only difference between the two materials consists in the different number of CH_2 groups in the tail. However, the difference in both phase sequence and dielectric properties is quite remarkable. This supports the suggestion of strong, sometimes crucial influence of non-polar tails on the dielectric properties of LC materials.

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DIELEKTRYCZNE WŁASNOŚCI FERROELEKTRYCZNEGO CIEKŁEGO KRYSZTAŁU Z CHIRALNĄ FAZĄ NEMATYCZNĄ

Streszczenie

Dielektryczne badania ferroelektycznego związku ciekłokrystalicznego 1H3R z nematyczną fazą chiralną przeprowadzono w obszarze niskich częstości.

Procesy relaksacyjne zarejestrowano jedynie w fazie ferroelektrycznej (mode Goldstona) oraz w fazie SmB* w obszarze częstości 60÷90 Hz. Przedstawiono charakterystyki zarejestrowanych procesów relaksacyjnych.