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MAREK WOJCIECHOWSKI,[1,2] MARZENA TYKARSKA[3] GRZEGORZ W. BĄK[2]

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

DIELECTRIC AND OPTICAL PROPERTIES OF LIQUID CRYSTAL 1H6Bi

Recently synthesized antiferroelectric liquid crystal 1H6Bi shows special optical properties related to change in handedness of the ferroelectric helix. The broadband dielectric measurements of this compound has been carried out, a number of dielectric relaxation modes corresponding to various temperatures and LC phases have been detected. The characteristic parameters of these modes are presented and compared with the optical data.

Keywords: antiferroelectric LC, dielectric relaxations, optical handedness.

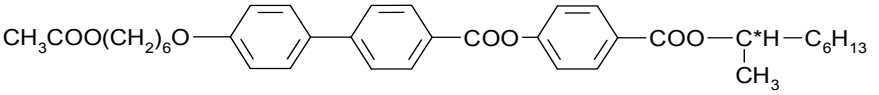
1. INTRODUCTION

Antiferroelectric liquid crystals show not only chiral smectic phases i.e. ferroelectric SmC* and antiferroelectric SmC^*_A phase, but frequently also a number of chiral subphases (SmC^*_α, SmC^*_β, SmC^*_γ) [1]. In these phases and subphases collective molecular relaxation processes exist and can be detected by broadband dielectric spectroscopy. In the SmA* phase a soft mode [2-4] and in the SmC* soft mode and Goldstone mode [2-5] are usually found. In the SmC^*_A phase two relaxation modes P_L and P_H can be detected, both these modes are related to the in-phase and to the anti-phase azimuthal angle fluctuations of the directors of the antitilted molecules in successive layers, respectively [5-7]. In the ferrielectric subphases situation is most complicated and still need a new experimental results.

In this work the dielectric and optic characteristics of recently synthesized antiferroelectric liquid crystalline compound 1H6Bi are presented and discussed. The temperature dependence of dielectric characteristics are compared with temperature dependence of helical pitch for all investigated phases of 1H6Bi compound. In the investigated compound the ferroelectric and antiferroelectric phases are suggested to exists.

2. EXPERIMENTAL

Molecular structure of the investigated antiferroelectric compound 1H6Bi is presented below.



(S)

The investigated compound was synthesized in the Institute of Chemistry, Military University of Technology (Warsaw) [8]. The material exhibits the ferroelectric phase in a comparatively broad temperature range. The phases sequence in this compound is as follows [8]:

Cr. 66.7 (SmC^*_A 48.0) SmC* 104.9 SmA 117.3 Izo.

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 in the smectic layers plane. The measurements were carried out with Solartron 1260 A Impedance Analyser with Chelsea Dielectric Interface in the frequency range 10^{-3} Hz ÷ $5 \cdot 10^5$ 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 values of the helical pitch were calculated from equation $p = \lambda/kn$, where λ – wave length of selective light reflection, n – average refractive index, $k = 1$ for the SmC^*_A phase and $k = 2$ for SmC* phase. The measurements of the helical pitch and helical twist sense were performed by methods described in [9].

3. RESULTS AND DISCUSION

The temperature dependencies of the real part of dielectric permittivity for two constant frequencies 1 kHz and 10 kHz are shown in Fig. 1. We chose the frequency 1 kHz because the registered relaxation processes exist close to this frequency region. The data corresponding to 1 kHz are compared with the data for 10 kHz. This temperature dependence reflects phase sequence upon cooling.

During the cooling process of the liquid crystalline sample from the SmA* phase to the ferroelectric SmC* phase a strong relaxation mode occurs and gives a large contribution to the dielectric constant. This is a classical Goldstone mode (GM).

On further cooling it is seen that in the temperatures near phase transition SmC^*-SmC^*_A, the dielectric constant changes dramatically, which suggests that the Goldstone mode disappears and the new relaxation process or processes in this temperature range occur. On further cooling an antiferroelectric phase appears with practically constant dielectric permittivity.

The dielectric parameters obtained from Havriliak-Negami equation were calculated separately for each of detected phases, i.e. fitted into single or double relaxation peaks in the particular case. The obtained results for the ferroelectric phase are shown in Fig. 2 and Fig. 3, Fig. 2 shows dielectric permittivity for various temperatures in the ferroelectric phase as a function of frequency. It shows the dielectric loss peaks for the Goldstone mode at three different temperatures.

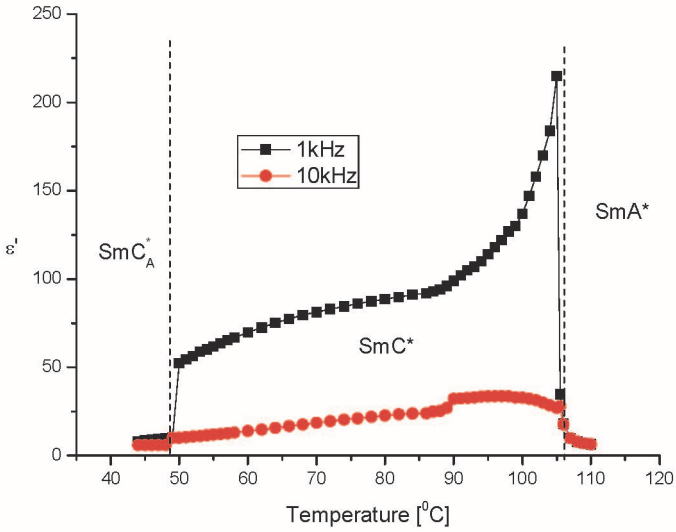


Fig. 1. Real part of dielectric permittivity vs. temperature for the whole temperature range investigated at the 1 kHz and 10 kHz frequencies.

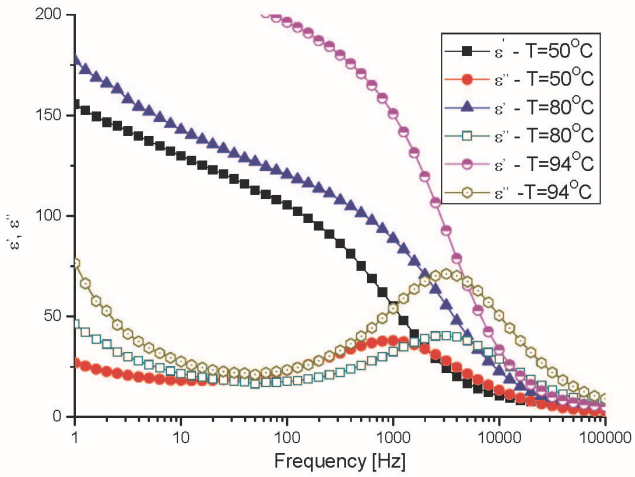


Fig. 2. Real and imaginary part of dielectric permittivity for chosen temperatures in the SmC* phase as a function of frequency.

Fig. 3 shows both the dielectric strength and the relaxation frequency calculated from Havriliak-Negami equation for different temperatures of the SmC* phase. The mode detected in this temperature range is Goldstone mode. As seen from the figure, the relaxation frequency of Goldstone mode increases with cooling process up to about 90ºC and possesses its maximum value at about 2.5 kHz at this temperature, then going down, near linearly, to about 0.5 kHz with further goes down cooling to SmC^*_A phase.

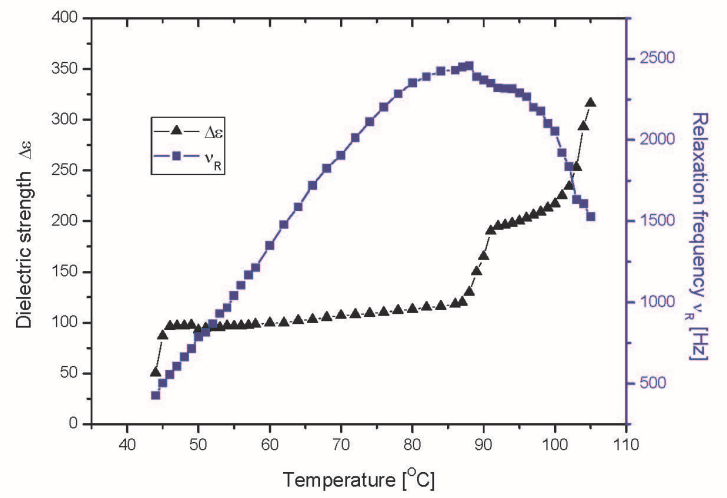


Fig. 3. Temperature dependence of dielectric strength and relaxation frequency of Goldstone mode in the ferroelectric phase of investigated compound.

The strong increase of the relaxation frequency with decreasing temperature and then nearly linear decrease with decreasing temperature is not a typical temperature dependence of the relaxation frequency of the Goldstone mode.

The dielectric strength of the Goldstone mode (Fig. 3) changes from about $\Delta\varepsilon = 320$ near the phase transition to the SmA* phase to about $\Delta\varepsilon = 50$ at 45ºC. The dielectric strength of GM has its maximum at the temperature of phase transition SmA*-SmC* and rapidly decreases with decreasing temperature to about $\Delta\varepsilon = 125$ at the temperature 87ºC and then slowly decreases to about $\Delta\varepsilon = 100$ at 47ºC and the temperature dependence is nearly linear in the temperature range between 87ºC÷47ºC.

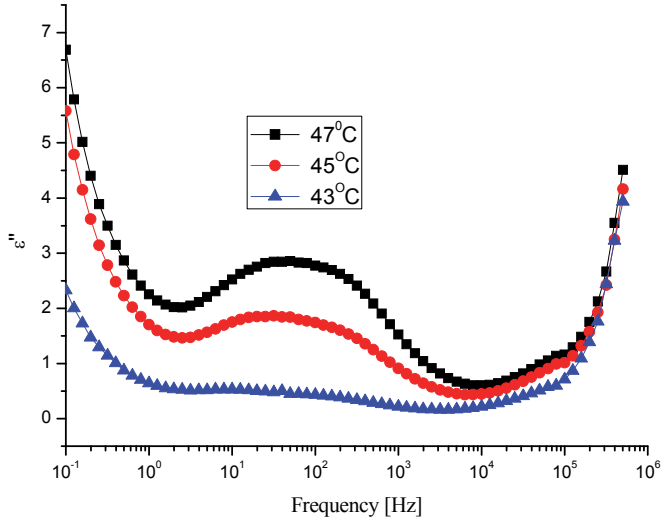


Fig. 4. Relaxation modes (AMF1 and AMF2) detected in the antiferroelectric phase of 1H6Bi compound at 43°C, 45°C and 47°C.

The SmC*$_A$ phase is the next one which appears on further cooling. Two weak relaxation modes were detected in this phase. The first one close to 100 kHz (AMF2) and the second one less than 0.1 kHz (AFM1). The relaxation peaks are presented in Fig. 4 for three temperatures corresponding to the antiferroelectric phase. The temperature dependencies of the relaxation frequencies of these two modes are presented in Fig. 5. The antiferroelectric phase detected in the investigated compound is observed in relatively narrow temperature range about 5 C wide and only in the cooling process. The relaxation frequency of AFM1 mode changes in the range between 40÷80 Hz (Fig. 5). The points in this figure are strongly dispersed for both modes, but much stronger for AFM2 mode. This frequency range corresponds to the temperature range of the low temperature part of P_L mode [10] for 4F6Bi compound and was also reported in our paper describing properties of 4F5Bi(2F) compound [11]. The relaxation frequencies of AFM2 mode change in the range between 40÷60 kHz (Fig. 5) in the temperature range of SmC*$_A$ phase and its relaxation frequency do not change significantly with temperature. The dielectric strength of this mode (Fig. 6) also remains constant and equal to 0.5 in the range of SmC*$_A$ phase. The high-frequency mode was observed in a lot of antiferroelectric materials [6, 10, 12, 13] and interpreted as relaxation of P_H mode, though the frequency range reported was somewhat higher, in the range between 200÷800 kHz.

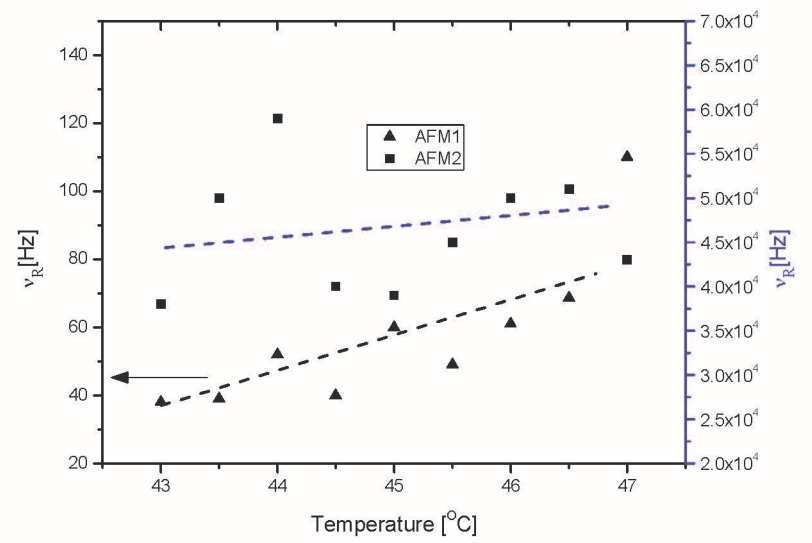


Fig. 5. Comparison of relaxation frequency of AFM1 and AMF2 modes detected in the antiferroelectric phase of 1H6Bi compound.

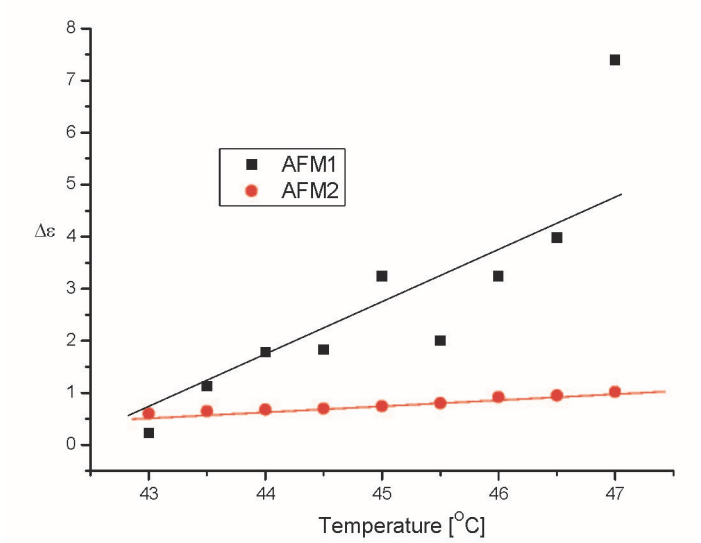


Fig. 6. Comparison of dielectric strength of AFM1 and AMF2 modes detected in the antiferroelectric phase of 1H6Bi compound.

The helical pitch of the investigated compound was calculated from measurements of wavelength of selectively reflected light as a function of temperature [9] and presented in Fig. 7. The helical pitch of 1H6Bi rapidly grows with decreasing temperature in the ferroelectric phase and at the temperatures below 80^0C the values of the pitch are outside the available range of the spectrophotometer. The handedness of the helix in 1H6Bi was established from miscibility studies with 2H6Bi [9] and the helix in both the SmC* and SmC^*_A phases turned out to be right-handed. The measurements of optical rotation were carried out for 1H6Bi in the temperature range in which the helical pitch is outside the measurement range of spectrophotometer. The measurements show that at the temperature 59ºC the handedness changes to the left-handed. It means that in this compound the change of the helix handedness occurs twice, the first change takes place within the SmC* phase and the second one at the point of transition to the SmC^*_A phase [9].

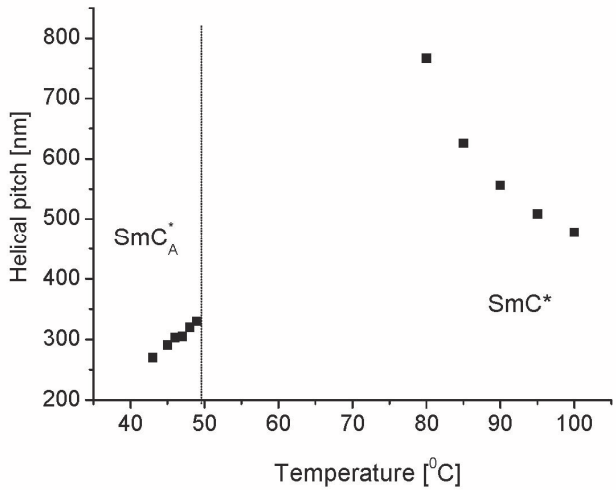


Fig. 7. Helical pitch in the ferroelectric and antiferroelectric phases in the investigated compound vs. temperature.

To compare the optical and dielectric results in the ferroelectric phase we analysed temperature dependence of dielectric parameters presented in Fig. 3 and the temperature dependence of the helical pitch (Fig. 7). The significant change of the dielectric parameters at 90ºC take places as show in Fig. 3, while no detectable anomaly in the temperature dependence of the helical pitch was observed (see Fig. 7). On the other hand the registered at 59ºC change in handedness of the ferroelectric helix is not observed in the dielectric results.

In the ferroelectric phase, the dielectric strength and the relaxation frequency of the Goldstone mode can be written as [14]:

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

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

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

$$K_{33} = \frac{p^2}{8\pi^2\varepsilon_0\Delta\varepsilon_G}\left(\frac{P_S}{\theta}\right)^2$$

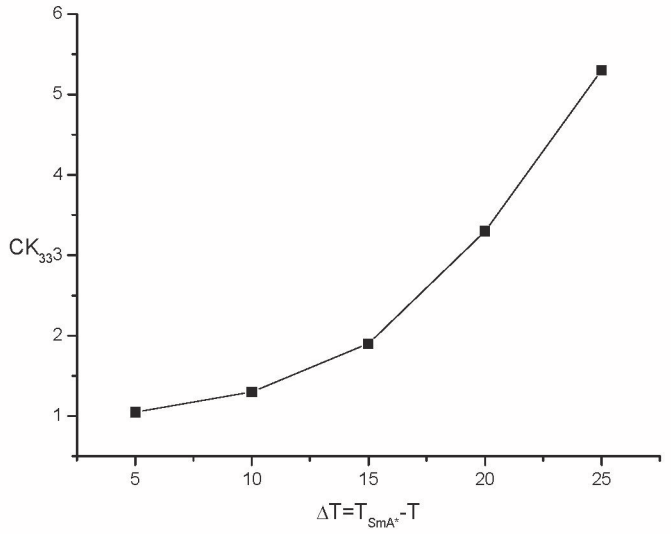


Fig. 8. Value proportional to twist elastic constant versus reduced temperature.

If we assume that the ratio P_S/θ is temperature-independent [13, 14] we can calculate the temperature-dependence of the elastic constant K_{33} having the helical pitch p. The relation CK_{33} vs. temperature (C is the proportionality constant) is presented in Fig. 8. It results from this figure that K_{33} rapidly grows when temperature decreases from the phase transition temperature SmA*-SmC*.

It means that the temperature dependencies of helical pitch and the dielectric strength of the Goldstone mode do not compensate and result in strong temperature dependence of CK_{33}. The above conclusion is in contradiction to results presented in paper [16], were K_{33} was found to be approximately temperature independent except for the temperature range near the phase transition to SmA* phase. It seems that the temperature dependence of K_{33} resulting from the optical and dielectric measurements and presented in Fig. 8 should be a subject of further investigations.

CONCLUSIONS

1) The dielectric study shows, that the recently synthesized 1H6Bi compound exhibits the ferroelectric phase in the broad temperature range and the antiferroelectric phase in comparatively narrow temperature range. The antiferroelectric phase is detected only in cooling process.
2) In the SmC* phase the strong Goldstone mode (maximum dielectric strength about 350) was observed. This phason mode exists due to the fluctuation of the phase angle.
3) In the SmC^*_A phase two weak relaxation mode were detected. The modes are suggested to be the P_L and P_H relaxation modes which are probably related to in-phase and anti-phase azimuthal angle fluctuation of the directors in the anti-tilted molecular pairs respectively.
4) Helical pitch shows strong temperature dependence in the ferroelectric phase and change sign of handedness in the region of this phase.
5) The temperature dependencies of helical pitch and dielectric strength of the Goldstone mode do not compensate each other and give strong temperature dependence of twist elastic constant K_{33}.

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DIELEKTRYCZNE I OPTYCZNE WŁAŚCIWOŚCI CIEKŁEGO KRYSZTAŁU 1H6Bi

Streszczenie

Ostatnio zsyntetyzowany antyferroelektryczny ciekły kryształ 1H6Bi wykazuje szczególne właściwości optyczne związane ze zmianą znaku skręcalności helisy ferroelektrycznej. W pracy przedstawiono wyniki badań dielektrycznych związku 1H6Bi. W obrębie fazy ferroelektrycznej i antyferroelektrycznej zarejestrowano kilka modów relaksacyjnych i przedstawiono ich charakterystyki. Otrzymane wyniki badań dielektrycznych porównano z wynikami badań optycznych badanego związku.