Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Biradarf, A. M. , Wróbel, S. and Haase, W.(1989) 'Dielectric studies of a ferroelectric liquid crystal', Liquid Crystals, 5: 4, 1227 — 1232

To link to this Article: DOI: 10.1080/02678298908026428

URL: http://dx.doi.org/10.1080/02678298908026428

LIQUID CRYSTALS, 1989, VOL. 5, NO. 4, 1227–1232

Dielectric studies of a ferroelectric liquid crystal

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Measurements of the complex dielectric permittivity in the frequency range 30 Hz–13 MHz have been made for the chiral smectic C and smectic A phases of the mixture ZLI-3654. In the S_C^* phase a large contribution to the electric permittivity coming from the Goldstone mode was found. For the pretransitional region S_C^*–S_A, only the soft mode has been detected. It is found that the molecular relaxation originating from the reorientation around the short axis is well separated from the soft mode even in the pretransitional region. The influence of different relaxation modes on the dielectric anisotropy is presented.

1. Introduction

Dielectric properties of ferroelectric liquid crystals have been studied extensively both theoretically and experimentally since 1975 when Meyer and coworkers [1] proved the existence of spontaneous polarization for the compound known as DOBAMBC. In a few papers [2–7] the dielectric studies of this material have been reported and two important relaxation modes, i.e. the Goldstone and the soft modes [8, 9], have been found. It was shown that the Goldstone mode appears in the S_C^* phase because of the phase fluctuations in the azimuthal orientation of the director. The soft mode shows up in the S_C^* phase, and a few degrees above the S_C^*–S_A transition due to the fluctuations in the amplitude of the tilt angle.

DOBAMBC is a compound with a low spontaneous polarization (around $15\,\mu\mathrm{C\,cm^{-2}}$). Recently, new materials have been synthesized [10, 11] that exhibit very high spontaneous polarization as well as a high static electric permittivity. In this paper we present the dielectric properties of a room-temperature ferroelectric liquid crystal as a function of frequency and temperature. The room-temperature ferroelectric liquid-crystal mixture is available from E. Merck, Darmstadt (code name ZLI-3654). The phase sequence for this mixture is

$$C_r \xleftrightarrow{\leq -30^\circ\mathrm{C}} S_C^* \xleftrightarrow{62^\circ\mathrm{C}} S_A \xleftrightarrow{76^\circ\mathrm{C}} \mathrm{Ch} \xleftrightarrow{86^\circ\mathrm{C}} \mathrm{I}.$$

Preliminary data regarding the spontaneous polarization, tilt angle, helical pitch, response time, and dielectric anisotropy have been reported [12] for this mixture. A detailed experimental and theoretical investigation related to soft mode for this mixture is given elsewhere [13].

2. Experimental method

The complex electric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured in sandwich-type cells. Gold-plated glass plates were used as electrodes, and the dielectric measurements

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were made in a shielded plate condenser described previously [14]. The distance between the plates was approximately 25 μm. Measurement cells were first calibrated using air and toluene as standards to calculate the absolute values of electric permittivity. Two principal alignments of the sample (planar and homoetropic) were achieved by putting the cell into a magnetic field of 1·2 T and then slowly cooling from the isotropic to the S_C^* phase with a cooling rate of 3 K h^{-1}. The quality of alignment was checked with a polarizing microscope and by watching the time development of the dielectric anisotropy. The two principal components of the electric permittivity tensor ($\varepsilon_\parallel^*$ and $\varepsilon_\perp^*$) were measured for the parallel (homoetropic) and perpendicular (planar) configurations [13] respectively.

Two different set-ups were used: for frequencies up to 13 MHz, the self-balancing Hewlett–Packard Bridge 4192 A under computer control, and for frequencies in the range 30 Hz–500 Hz the General-Radio Bridge 1651 A with oscillator 1310 and detector 1232 A, based upon the transformer-ratio-arm principle.

3. Results and discussion

The complex electric permittivity has been measured over wide temperature and frequency ranges. In the following subsections the results of these measurements are reported and discussed.

3.1. *Goldstone-mode contribution to the $\varepsilon_\perp$ component*

Figure 1 shows the frequency dependences of the real part $\varepsilon'_\perp$ of the complex electric permittivity at different temperatures. As may be seen, the electric permittivities measured at low frequencies are very high and strongly temperature-dependent. However, the relaxation frequency over the whole S_C^* phase was found to be more or less independent of temperature, which is in good agreement with theory. Above the transition temperature (S_C^*–S_A) there is practically no contribution to the Goldstone mode originating from the spontaneous polarization. We should stress that the dispersion curves obtained in this study are qualitatively very similar to those obtained

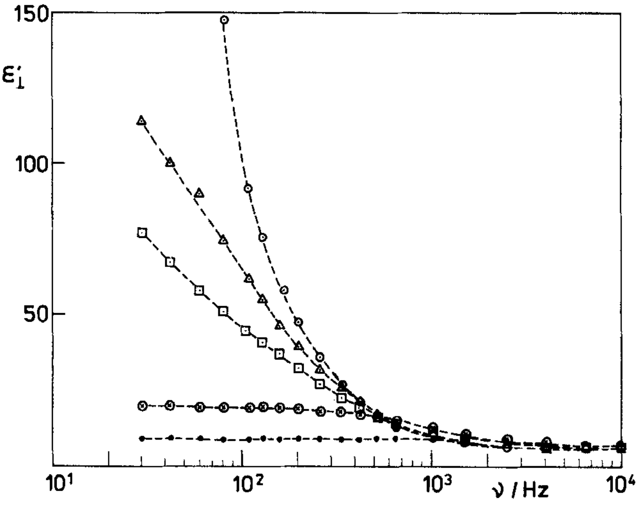


Figure 1. Frequency dependence of the Goldstone-mode contribution to $\varepsilon_\perp$ obtained at different temperatures: ○, 45·6°C; △, 57·5°C; □, 59·1°C; ⊗, 59·7°C; ●, 60·0°C.

for other ferroelectric materials [2, 3, 4, 6], except for the fact that our material shows very high electric permittivity and the measurements have been extended to the low-frequency range. The measurements could not be extended to the sub-hertz region owing to the pronounced conductivity contribution, which is also strongly temperature-dependent.

3.2. *Soft-mode contribution to* $\varepsilon_{\perp}$

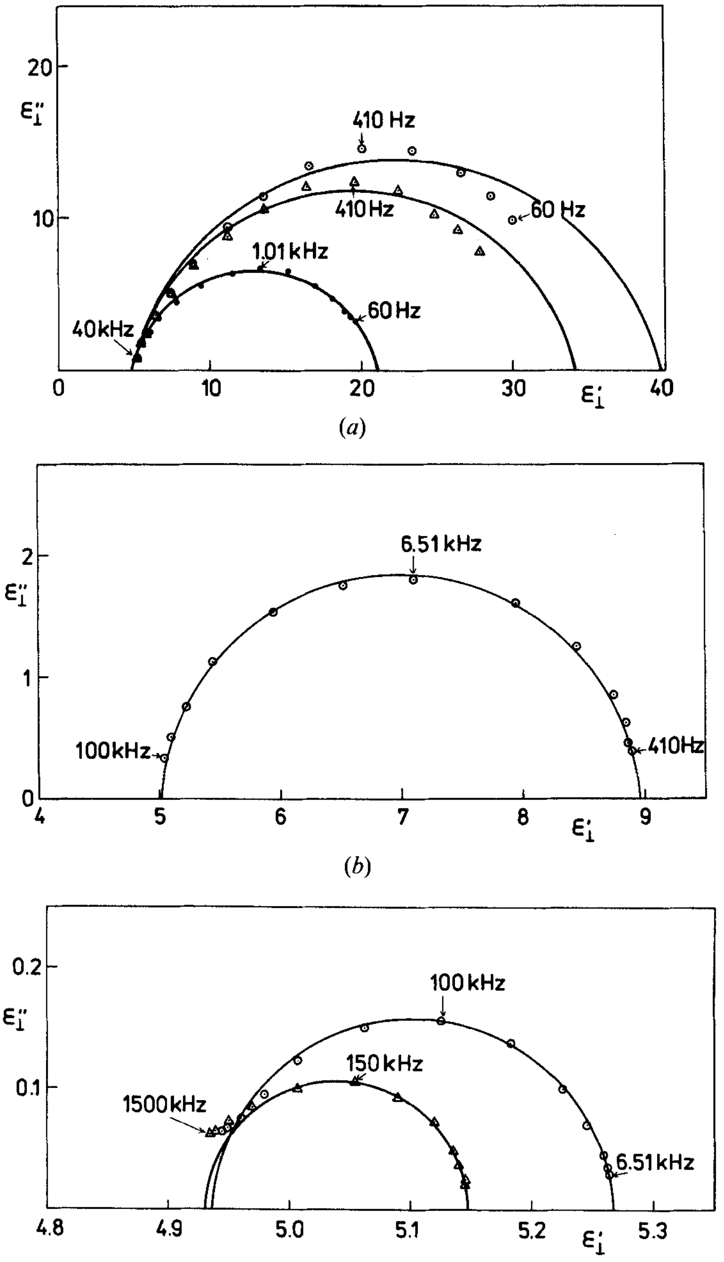
As can be seen in figure 1, in the S_C^* phase there is a pronounced dispersion region below 1 kHz connected with the Goldstone mode. However, if the $\varepsilon'_{\perp}$ scale is magnified (see figure 2*a*), a new dispersion region shows up, associated with the soft mode above 59·8°C (59·8°C is the transition temperature where the Goldstone-mode contribution is negligible), but the dispersion takes place at much higher frequencies (from 1 kHz to 1 MHz) in comparison with the Goldstone mode. Additionally, the soft-mode dielectric increment in this pretransitional region is strongly temperature-dependent (see figures 2*b*, *c*) and vanishes a few degrees above 62°C, which is the S_C^*–S_A transition determined from texture observations [12]. It is evident from figures 2 (*a*–*c*) that the Goldstone mode appears up to 59·7°C and the soft mode starts to appear from 59·8°C because the relaxation frequency suddenly jumps from 410 Hz to 1·01 kHz. This means that the ferroelectric phase transition lies between 59·7 and 59·8°C. In order to experimentally confirm the existence of these two modes in such a narrow temperature range, high-resolution temperature measurements are needed. It is known that texture observations always give the highest transition temperature. However, a difference of about 2°C seems to be too high. In our case we might also think of a biphasic region observed for other mixtures. It is worth noting that the difference between the dielectric phase transition and that found by texture studies is also observed for DOBAMBC [6].

3.3. *Dispersion of the* $\varepsilon_{\parallel}$ *component*

As for polar liquid crystals, two principal molecular reorientations, i.e. the reorientations around the short and long molecular axes, give separate dielectric relaxation regions falling within the radio and microwave frequency region [15, 16]. The dispersion measurements made by us for the $\varepsilon_{\parallel}^*$ component revealed the existence of low-frequency molecular relaxation in both smectic phases. Figure 3 shows the loss factor versus frequency in the chiral smectic C and A phases. As can be seen, the critical frequencies of the molecular relaxation are much higher than those obtained for the Goldstone and the soft modes. It is worth pointing out that the molecular relaxation exhibits a distribution of relaxation times that is consistent with the results obtained for other liquid-crystalline mixtures [16]. The activation energies calculated for the low-frequency molecular relaxation are about 100 kJ mol^{-1} in both phases, which is typical of smectic C and A phases [15, 16].

3.4. *Dielectric anisotropy*

To describe the anisotropic properties of liquid crystals, like nematics, we must specify the values of their material parameters along two directions: parallel and perpendicular to the director **n** which is the average direction of the molecular long axes. To characterize the anisotropy of a given physical quantity, a parameter called



(*a*)

(*b*)

(*c*)

Figure 2. (*a*) Cole–Cole representation for the Goldstone mode (⊙, 59·6°C; △, 59·7°C) and soft mode (● = 59·8°C). (*b*) Cole–Cole representation for the soft mode contribution at 60°C (⊙). (*c*) Cole–Cole representation for the soft mode at 62·0°C (⊙) and 62·9°C (△) (solid lines are Cole–Cole function fits).

the anisotropy is frequently introduced; this is defined as the difference between the values measured along the direction of **n** and perpendicular to it.

The frequency dependences of $\varepsilon_\parallel$ and $\varepsilon_\perp$, the components of the electric permittivity tensor, as well as the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$) measured for the S_C^* phase

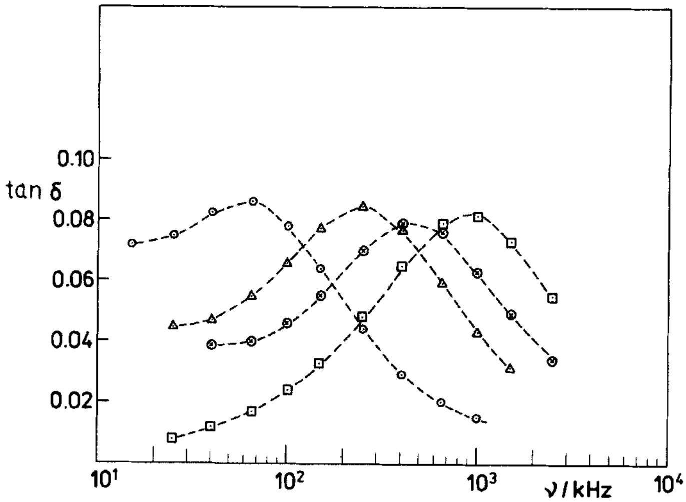


Figure 3. Frequency dependence of the tangent delta (loss factor) ($\tan\delta = \varepsilon''/\varepsilon'$) for the molecular relaxation at different temperatures in the parallel orientation in the S_C^* and S_A phases: ⊙, 32·0°C; △, 47·4°C; ⊗, 55·2°C; ☐, 62·8°C.

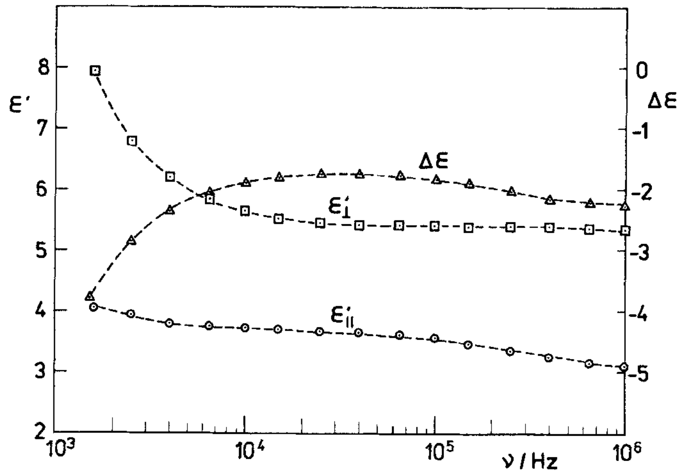


Figure 4. Dielectric permittivities $\varepsilon_\perp$ (☐) and $\varepsilon_\parallel$ (⊙) and dielectric anisotropy. $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ (△) versus frequency at 47·4°C.

at 47°C in the frequency range 1 kHz–1 MHz, are shown in figure 4. As we can see, the $\varepsilon_\parallel$ component exhibits a low-frequency dispersion region with critical frequency of about 100 kHz, which is in good agreement with the preliminary dielectric measurements for this mixture [12]. As we have discussed, this dispersion region is connected with the well-known molecular reorientation about the short molecular axis. On the other hand, the $\varepsilon_\perp$ component is frequency-independent in the range 50 kHz–1 MHz because this component is influenced by the reorientation about the long axis of polar molecules. At frequencies below about 10 kHz there is a critical increase in the $\varepsilon_\perp$ component with decreasing frequency coming from the Goldstone-mode contribution. The frequency dependences of the $\varepsilon_\parallel$ and $\varepsilon_\perp$ components are reflected in the dielectric anisotropy, which is constant ($\Delta\varepsilon \approx -2$) in the high-frequency range (1 MHz), then increases to about $-1\cdot 8$ owing to low-frequency molecular relaxation, and then eventually decreases critically (below 10 kHz) because of the Goldstone-mode contribution.

4. Conclusions

(1) It has been found that in the S_C^* phase the $\varepsilon_\perp$ component exhibits a very large contribution coming from the Goldstone mode.

(2) The soft-mode contribution shows up only around the S_C^*–S_A (62°C) transition temperature. To study the soft-mode behaviour in the S_C^* phase, we should suppress the Goldstone mode by a static electric field [17], and such studies are in progress.

(3) In the low-frequency range the dielectric anisotropy is dominated by the Goldstone mode.

(4) The dielectric relaxation in the parallel orientation is due to molecular reorientation around the short axis.

The authors sincerely thank the E. Merck for supplying the material. Fruitful discussions with Drs T. Geelhaar (E. Merck) and F. J. Bormuth (TH) are gratefully acknowledged. One of the authors (AMB) thanks the DAAD for financial assistance. One of the authors (SW) is grateful to the Technische Hochschule, Darmstadt for financial support during his stay.

References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. Phys. Lett.*, **36**, L69.

[2] Ostrovski, B. I., Rabinovich, A. Z., Sonin, A. S., and Strukov, B. A., 1978, *Zh. éksp. teor. Fiz.*, **74**, 1448.

[3] Hoffmann, J., Kuczynski, W., and Malecki, J., 1978, *Molec. Crystals liq. Crystals*, **44**, 287.

[4] Zeks, B., Levstik, A., and Blinc, R., 1979, *J. Phys., Paris Colloq.*, **40**, C3–409.

[5] Benguigui, L. G., 1982, *J. Phys., Paris*, **43**, 915.

[6] Glogarova, M., Pavel, J., and Fousek, J.,1984, *Ferroelectrics*, **55**, 117.

[7] Levstik, A., Carlsson, T., Filipic, C., and Zeks, B., 1988, *Molec. Crystals liq. Crystals*, **154**, 259.

[8] Blinc, R., and Zeks, B., 1978, *Phys. Rev.* A, **18**, 740.

[9] Martinot-Lagarde, P., and Durand, G., 1981, *J. Phys.*, **42**, 269.

[10] Mohr, K., Kohler, S., Worm, K., Pelzl, G., Diele, S., Zaschke, H., Demus, D., Andersson, G., Dahl, I., Lagerwall, S. T., Skarp, K., and Stebler, B., 1987, *Molec. Crystals liq. Crystals*, **146**, 151.

[11] Bahr, C., Heppke, G., and Sharma, N. K., 1987, *Ferroelectrics*, **76**, 151.

[12] Geelhaar, T., 1987a, Private Communication from E. Merck (Darmstadt); 1987b, *Abstract of first International Symposium on Ferroelectric Liquid Crystals*, 21–23 September, Bordeaux-Arcachon, France, L.4.

[13] Biradar, A. M., Wróbel, S., and Haase, W., 1989, *Phys. Rev.* A, **39** (in the press).

[14] Haase, W., Pranoto, H., and Bormuth, F. J., 1985, *Ber. Bunsenges. phys. Chem.*, **89**, 1129.

[15] Parneix, J. P., Legrand, C., and Decoster, D., 1987, *Molec. Crystals liq. Crystals*, **98**, 361.

[16] Kresse, H., 1983, *Advances in Liquid Crystals*, Vol. 6, edited by G. H. Brown (Academic Press), p. 109.

[17] Ozaki, M., Nakao, K., and Yoshino, K., 1988, *Abstract of 12th International Liquid Crystals Conference*, 15–19 August, Freiburg, FRG, FE 33, p. 309.