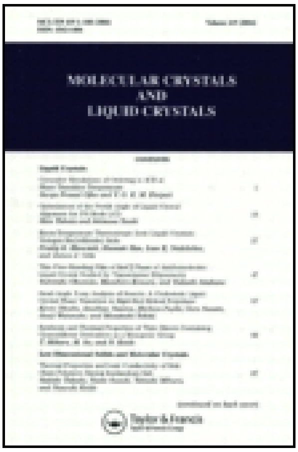


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Characterization of Collective Relaxation Modes of a Ferroelectric Mixture Through Dielectric Spectroscopy

Aanchal Dwivedi [a b], R. Dhar [b], V. K. Agrawal [a], R. Dabrowski [c] & D. Ziobro [c]

[a] Physics Department, University of Allahabad, Allahabad, India

[b] Centre of Material Sciences, Institute of Interdisciplinary Studies, Nehru Science Complex, University of Allahabad, Allahabad, India

[c] Institute of Chemistry, Military University of Technology, Warsaw, Poland

Version of record first published: 30 Jun 2011

To cite this article: Aanchal Dwivedi, R. Dhar, V. K. Agrawal, R. Dabrowski & D. Ziobro (2011): Characterization of Collective Relaxation Modes of a Ferroelectric Mixture Through Dielectric Spectroscopy, Molecular Crystals and Liquid Crystals, 541:1, 262/[500]-269/[507]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.569252

Mol. Cryst. Liq. Cryst., Vol. 541: pp. 262/[500]–269/[507], 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.569252

Characterization of Collective Relaxation Modes of a Ferroelectric Mixture Through Dielectric Spectroscopy

AANCHAL DWIVEDI,[1,2] R. DHAR,[2] V. K. AGRAWAL,[1]
R. DABROWSKI,[3] AND D. ZIOBRO[3]

[1]Physics Department, University of Allahabad, Allahabad, India
[2]Centre of Material Sciences, Institute of Interdisciplinary Studies, Nehru Science Complex, University of Allahabad, Allahabad, India
[3]Institute of Chemistry, Military University of Technology, Warsaw, Poland

Molecular motion of a ferroelectric mixture has been studied by the dielectric spectroscopy in the frequency range of 1 Hz to 35 MHz in different mesophases viz. chiral nematic (N^*), ferroelectric (SmC^*) and hexatic (SmI^*) phases. One soft like relaxation process in the N^* phase and usual Goldstone mode in the SmC^* phase have been found. A new mode has been detected at ~50 Hz in the vicinity of SmC^*-SmI^* phase transition. The dielectric strength of this mode is highly temperature dependent and increases as temperature decreases. Two modes in different frequency ranges (kHz and few hundred Hz ranges) have been detected in the SmI^* phase.

Keywords Bond orientation order; goldstone mode; hexatic phase; soft mode

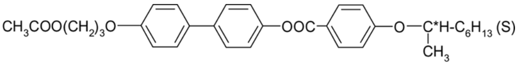
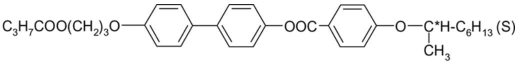
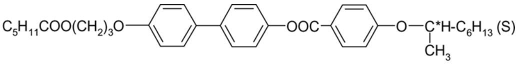
1. Introduction

Smectic liquid crystalline materials have many significant advantages over the nematic liquid crystals viz. low birefringence, low viscosities and high spontaneous polarization as they have a great potential for application in flat panel displays (FPDs). The option of ferroelectricity in liquid crystals was pointed out by Meyer from symmetry considerations [1]. Although most of the tilted smectic phases fulfill the symmetry requirements for ferroelectricity, but the smectic C^* phase is more appropriate for FPDs, due to its low rotational viscosity (γ). Along with SmC^* phase, chiral hexatic phases are also important due to its interesting ferroelectric and linear dielectric properties [2,3]. Hexatic phases are generally seen at the lower temperature (below the chiral smectic phases viz. ferroelectric SmC^*, antiferroelectric SmC_A^*). These phases exhibit one-dimensional positional order along the layer normal as well as long bond-orientational order within the layers. However, in the last three decades number of papers on hexatic ferroelectric liquid crystals are

---

Address correspondence to R. Dhar, Centre of Material Sciences, Institute of Interdisciplinary Studies, Nehru Science Complex, University of Allahabad, Allahabad-211002, India. Tel.: +91-9415278539; Fax: +91-532-2466122; E-mail: dr_ravindra_dhar@hotmail.com low in comparison to papers on ferroelectric SmC* phase. There are many reasons behind this. One of them is that the hexatic phases in most of the cases, are found to be monotropic [4–6] and sometimes their temperature range is very narrow.

In the present work, we report the temperature and frequency dependent dielectric properties of a tri-component ferroelectric mixture (A2) which exhibited both the ferroelectric SmC* and hexatic SmI* phases. The molecular formula along with their mole fraction of all the three components of the mixture A2 is given below:

Component 1	4′-(3-etanoyloxyprop-1-oxy)biphenyl-4-yl (S)-4-(1-methylheptyloxy)benzoate 	Mole fraction = 0.51
Component 2	4′-(3-butanoyloxyprop-1-oxy)biphenyl-4-yl (S)-4-(1-methylheptyloxy)benzoate 	Mole fraction = 0.31
Component 3	4′-(3-capronoyloxyprop-1-oxy)biphenyl-4-yl (S)-4-(1-methylheptyloxy)benzoate 	Mole fraction = 0.18

The phase sequence with transition temperatures, obtained by DSC at the scan rate 5.0 K/min (in the cooling cycle) of the mixture A2 is as follow:

$$\mathrm{I} - (96.6^\circ\mathrm{C}) \rightarrow \mathrm{N}^* - (79.2^\circ\mathrm{C}) \rightarrow \mathrm{SmC}^* - (58.8^\circ\mathrm{C})\mathrm{SmI}^* - (43.3^\circ\mathrm{C}) \rightarrow \mathrm{Cr}$$

2. Experimental Techniques

The complex dielectric permittivity ($\varepsilon_\perp^* = \varepsilon_\perp' - j\varepsilon_\perp''$) of the planar aligned sample of thickness 8.7 μm, has been measured in the frequency range of 1 Hz to 35 MHz using phase sensitive multimeter N4 L (model PSM 1735), coupled with an impedance analysis interface. The electrodes of the dielectric cell are gold coated. The temperature of the sample was controlled with the help of a hot stage (Instec HS-1) with an accuracy of ± 0.1°C. A measuring alternating electric field of 0.1 $\mathrm{V_{rms}}$ was applied across the sample. The data have been acquired during the cooling cycle of the sample from its isotropic phase.

In order to analyze the measured data, the dielectric spectra has been fitted with the generalized Cole-Cole equation [7],

$$\varepsilon_\perp^* = \varepsilon_\perp' - j\varepsilon_\perp'' = \varepsilon_\perp'(\infty) + \sum_i \frac{(\Delta\varepsilon_{\perp i})}{1 + (j(f/f_{R_i}))^{(1-h_i)}} + \frac{A}{f^n} - j\frac{\sigma_{ion}}{2\pi\varepsilon_0 f^k} - jBf^m \tag{1}$$

Here $\Delta\varepsilon_{\perp i}$ $(= \varepsilon_\perp'(0) - \varepsilon_\perp'(\infty))$, f_{Ri}, h_i are the dielectric strength, relaxation frequency and symmetric distribution parameter ($0 \le h_i \le 1$) of the ith mode respectively. $\varepsilon_\perp'(0)$ and $\varepsilon_\perp'(\infty)$ are the low and high frequency limiting values of the relative dielectric permittivity respectively. The third and fourth terms of Eq. (1) represent the contribution of electrode polarization capacitance and ionic conductivity (σ_{ion}), respectively, at low frequencies [8,9]. The fifth term of Eq. (1) accounts for high

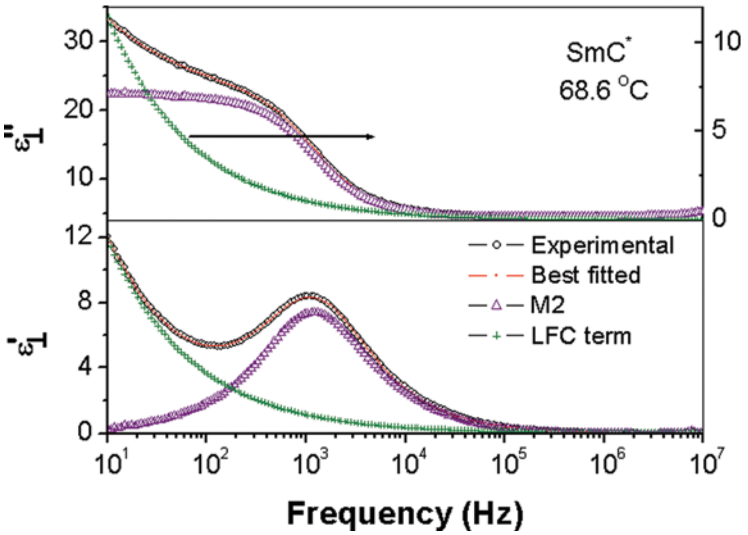


Figure 1. Frequency dependence of the dielectric permittivity ($\varepsilon'_\perp$) and dielectric loss ($\varepsilon''_\perp$) in the SmC* phase. Open circles show the experimental data, solid lines illustrate the best fitted curve on the Cole-Cole equation, open triangles show the Goldstone mode (M2) after subtracting the low frequency correction terms from experimental data and plus symbols show low frequency correction terms (on the secondary axis in the upper frame). (Figure appears in color online.)

frequency parasitic effects due to the ITO resistance and lead inductance [9–11]. A, B, m, n and k are the fitting constants. ε_0 (=8.85 pF/m) is the free space permittivity. In case of pure Ohmic conductivity $k = 1$. More details of experimental procedures are reported else where [12,13]. The dielectric parameters of all the relaxation modes in different phases are determined by fitting Eq. (1) to the experimental data. The low frequency correction term after fitting the experimental data of the SmC* phase are shown in Figure 1 for dielectric permittivity ($\varepsilon'_\perp$) and dielectric loss ($\varepsilon''_\perp$). The values of the correlation factor $R^2 = 0.99997$ and $\xi^2 = 0.00317$ confirm the best fit of experimental data with Eq. (1) and hence the reliability of the parameters.

3. Results and Discussion

Characteristic dielectric spectra of the SmC* is shown in Figure 1 whereas that of the N* and SmI* phases are shown in Figure 2. Figure 3 shows the temperature dependence of the relaxation frequencies of different modes observed in the N*, SmC* and SmI* phases. Figure 4 illustrates the temperature dependence of the dielectric strength for different relaxation modes observed for the mixture.

On cooling from the isotropic liquid phase, one relaxation phenomenon (M1) has been observed in chiral nemectic (N*) phase. The relaxation frequency (f_R) and dielectric strength ($\Delta\varepsilon_\perp$) of the mode M1 has been found to be temperature reliant. The f_R of mode M1 decreases continuously on cooling and varies between 2 MHz-200 kHz (see Fig. 3) within the N* phase. On the other hand $\Delta\varepsilon_\perp$ of the relaxation (M1) increases from 0.2 to 0.7 at the N*-SmC* transition (see Fig. 4). Distribution parameter (h) of the mode is found to be very small (~0) and remains

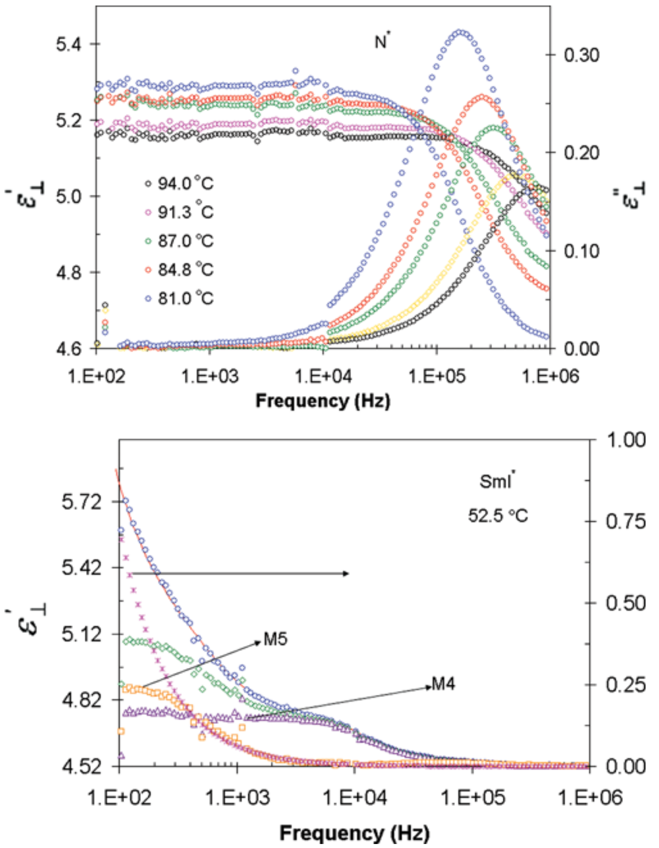


Figure 2. (a) Dielectric permittivity ($\varepsilon'_{\perp}$) and dielectric loss ($\varepsilon''_{\perp}$) curves at various temperatures of the chiral nematic (N*) phase; (b) Two relaxation phenomenon (M4 and M5) in forms of dispersion curves in SmI* phase at 52.5°C.

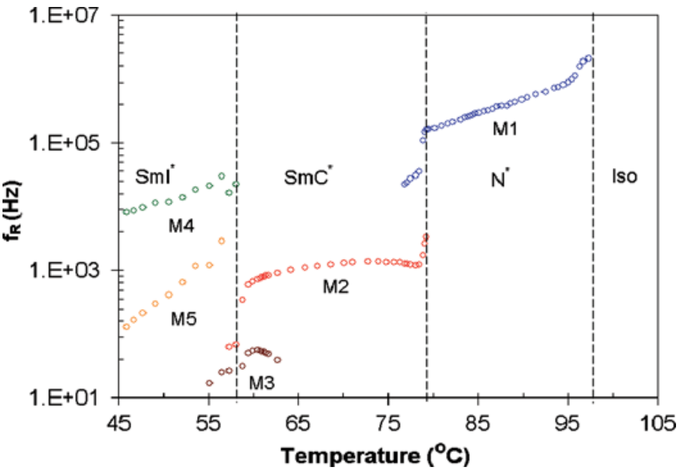


Figure 3. Variation of relaxation frequencies (f_R) of various relaxation modes with temperature.

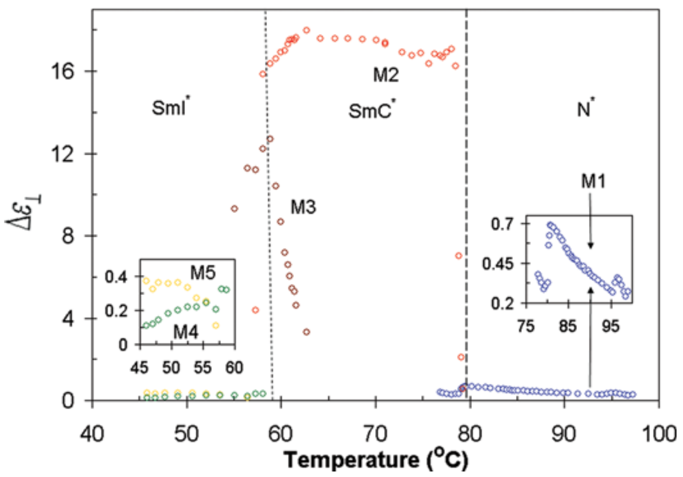


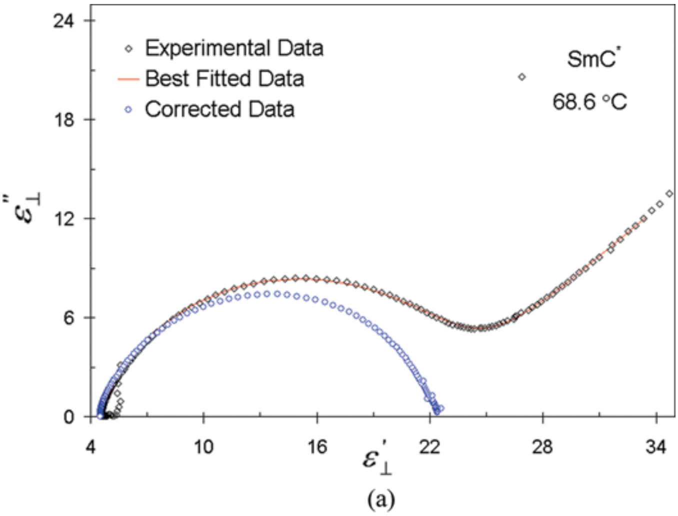
Figure 4. Variation of dielectric strength ($\Delta\varepsilon_\perp$) with temperature. The insets show the enlarged views of the modes M1, M4 and M5.

constant throughout the N* phase. The values of ionic conductivity (σ_{ion}) and constant k of the fourth term of Eq. 1, are found to be $\sim 1.3 \times 10^{-8}$ S m^{-1} and ~0.96 respectively at 92.5°C. The value of σ_{ion} decreases with temperature going down.

Relaxation process in the N* phase, with similar phase sequence, has been suggested as the Soft mode [14–16]. Soft mode appears due to fluctuations of the magnitude of the tilt angle of the director. Soft mode by definition, is a mode restoring the symmetry of the low temperature phase i.e., SmC*. From this definition, observed mode (M1) should not be called as Soft mode in the N* phase. A possible reason of its existence may be partial rotation of molecules about their short axis due to imperfect alignment.

The dielectric spectra of mode M1 of the chiral Nematic (N*) phase is shown in the Figure 2(a) as dispersion and absorption curves. The mode M1 has been observed even below N*-SmC* transition, but f_R and $\Delta\varepsilon_\perp$ decrease continuously and the mode almost disappear at ~77°C. This support Soft mode like behavior of mode M1 instead of individual molecular rotational behavior.

While going from N* to SmC* at ~79.3°C, a new relaxation mode (M2) appears (shown in Fig. 1). The $\Delta\varepsilon_\perp$ of the mode M2 increases with the decrease in the temperature. It increases from 0.6 to 17.5 and becomes constant for the stabilized SmC* phase. The f_R of the mode M2 is almost stable (~1.3 kHz) with temperature. On the basis of these characteristics, M2 is identified to be the Goldstone (phason) mode arising due to phase in the azimuthal orientation of the director [9,17]. However the $\Delta\varepsilon_\perp$ of the Goldstone mode (M2) in this case is low as compared to the other materials [18,19]. The distribution parameter (h) of the mode M2 is found to be higher (~0.1) than that of the mode M1 in the N* phase. Another mode (M3), in low frequency range (~50 Hz), has been detected in the vicinity of SmC*-SmI* transition beside the Goldstone mode. $\Delta\varepsilon_\perp$ of the mode M3 is highly temperature dependent and increases as temperature decreases (see Fig. 4). Its strength varies from 3.0 to 12.7 in SmC*. Figure 5(a) shows the Cole-Cole plot only for the Goldstone mode (M2) at 68.6°C whereas Figure 5(b) at 61.2°C reveals both the modes i.e., M2 and M3. The small semicircle of Figure 5(b) represents the mode M3; but its origin



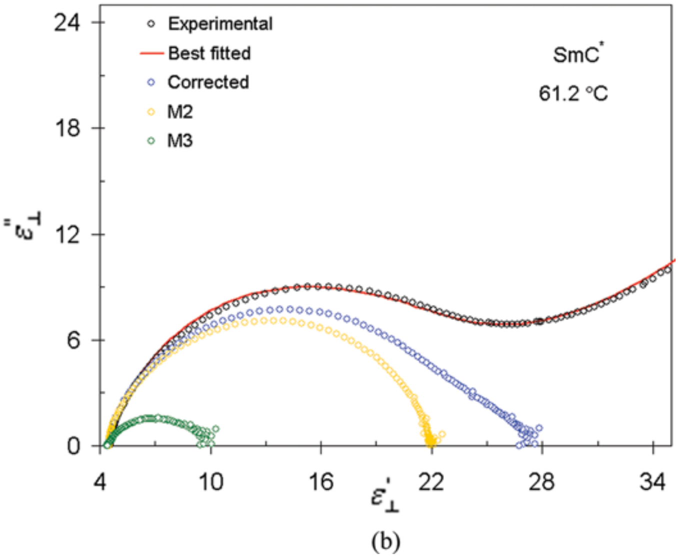


Figure 5. (a) Cole- Cole plot for the Goldstone mode (M2) in the SmC* phase at 68.6 °C; (b) Cole- Cole plots for the Goldstone mode (M2) near the SmC*-SmI* phase transition at 61.2°C. Small circle shows the mode M3.

has not been identified yet. The new mode M3 continues upto ~4°C below the SmC*-SmI* transition as seen in the Figures 3 and 4.

In the hexatic SmI* phase, mode M4 (f_R ~22.5 kHz) initially appears at 58.1°C. On further cooling another mode M5 (f_R ~2.9 kHz) appears at about 56.5°C. The relaxation frequency of both the modes (M4 and M5) decreases with decrease in temperature throughout the SmI* phase. Near crystallization (~45°C), the values of relaxation frequencies of the modes M4 and M5 are 8.1 kHz and 129 Hz respectively. $\Delta\varepsilon_\perp$ of mode M4 shows decreasing trend whereas that of the mode M5 shows increasing trend with decrease in temperature. The $\Delta\varepsilon_\perp$ of mode M4 decreases from

0.3 to 0.1, whereas that of the M5 increases from 0.1 to 0.4 on decreasing temperature. According to the range of the relaxation frequencies, these modes most probably attributed to Bond Orientation Order and tilt fluctuations [20,21]. The dispersion plots of both the dielectric processes (M4 and M5) found in SmI*, are shown in Figure 2(b).

4. Conclusions

Dielectric spectroscopy combined with the texture study of the ferroelectric mixture A2 confirms that the mixture possesses the phase sequence I-N*-SmC*-SmI*-Cr. The chiral nematic (N*) phase exhibits the Soft mode like behavior having temperature dependent relaxation frequency (f_R) and dielectric strength ($\Delta\varepsilon_\perp$). However, it does not follow Curie-Weiss law. Mode M1 penetrates in ferroelectric SmC* phase up to 3°C below the N*-SmC* transition and then after extinguishes. Goldstone mode has been observed in the SmC* phase with temperature independent relaxation frequency but temperature dependent dielectric strength ($\Delta\varepsilon$). A new relaxation mode has been detected in the vicinity of the SmC*-SmI* transition at ~50 Hz. Two dielectric relaxation modes M4 (22.5 kHz–8.1 kHz) and M5 (2.9 kHz–129 Hz) have been observed in the hexatic SmI* phase presumably due to Bond Orientation Order and tilt fluctuations.

Acknowledgment

One of us (A. D.) is thankful to CSIR (New Delhi) for granting a senior research fellowship.

References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., & Keller, P. (1975). *J. Phys. Lett. (Paris)*, *36*, L69.
[2] Schacht, J., Dierking, I., Giesselmann, F., Mohr, K., Zaschke, H., Kuczyński, W., & Zugenmaier, P. (1995). *Liq. Cryst.*, *19*, 151.
[3] Rychetský, I., Glogarová, M., & Novotná, V. (2003). *Phys. Rev. E.*, *67*, 021704.
[4] Pfeiffer, M., Wróbel, S., Beresnev, L. A., & Haase, W. (1991). *Mol. Cryst. Liq. Cryst.*, *202*, 193.
[5] Ghosh, A. K., Direking, I., & Haase, W. (2002). *Ferroelectrics*, *277*, 25.
[6] Mikulko, A., Marzec, M., Wierzejska, M., Douali, R., Legrand, Ch., Wróbel, S., Dabrowski, R., & Haase, W. (2006). *Phase Transitions*, *79*, 585.
[7] Cole, R. H., & Cole, K. S. (1941). *J. Chem. Phys.*, *9*, 341.
[8] Srivastava, S. L., & Dhar, R. (1991). *Indian J. Pure Appl. Phys.*, *29*, 745.
[9] Gouda, F., Skarp, K., & Lagerwall, S. T. (1991). *Ferroelectrics*, *113*, 165.
[10] Srivastava, S. L. (1993). *Proc. Natl. Acad. Sci. India*, *63*, 311.
[11] Dhar, R. (2004). *Indian J. Pure Appl. Phys.*, *42*, 56.
[12] Pandey, M. B., Dhar, R., Agrawal, V. K., Dabrowski, R., & Tykarska, M. (2004). *Liq. Cryst.*, *31*, 973.
[13] Dwivedi, Aanchal, Dhar, R., Pandey, M. B., Das, I. M. L., & Dabrowski, R. (2009). *J. Mol. Liq.*, *148*, 1.
[14] Hiller, S., Biradar, A. M., Wróbel, S., & Haase, W. (1996). *Phys. Rev. E.*, *53*, 641.
[15] Ismaïli, M., Bougrioua, F., & Isaert, N. (2001). *Phys. Rev. E.*, *65*, 011701.

[16] Rutkowska, J., Perkowski, P., Piecek, W., Raszewski, Z., & Kedzierski, J. (2008). *Opto-Electron. Rev.*, *16*, 262.

[17] Thakur, A. K., Bawa, S. S., Biradar, A. M., Kaur, S., & Annapoorni, S. (2005). *J. Appl. Phys.*, *97*, 084106.

[18] Wróbel, S., Mikulko, A., Douali, R., Legrand, Ch., Marzec, M., Haase, W., Isaert, N., & Ismaili, M. (2005). *Phase Transit.*, *78*, 905.

[19] Kumar, A., Dhar, R., Agrawal, V. K., Dabrowski, R., & Tykarska, M. (2008). *J. Appl. Phys.*, *104*, 054104.

[20] Rychetský, I., Pociecha, D., Dvořák, V., Mieczkowski, J., Górecka, E., & Glogarová, M. (1999). *J Chem. Phys.*, *111*, 1541.

[21] Novotná, V., Kašpar, M., Hamplová, V., Glogarová, M., & Rychetský, I. (2004). *Liq. Cryst.*, *31*, 1131.