Physical Sciences
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Dielectric and optical study of the ferroelectric liquid crystal mixture ZLI-3654

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Ferroelectric liquid crystals exhibit a variety of remarkable properties and show can find use in technical applications such as optical displays. Dielectric spectroscopy studies of these compounds provide data on their static and dynamic properties. In this study, the dielectric and optical behaviour of the ferroelectric liquid crystal mixture ZLI-3654 has been investigated in a temperature range of 30°C to 62°C. The dielectric constant and the dielectric loss of the mixture has been measured in different phases, in a frequency range of 100 Hz to 10 MHz on an impedance/gain phase analyzer. The dielectric study has exhibited relaxation behaviour giving rise to different relaxation frequencies for given temperatures. These have been used to calculate the relaxation time and activation energies in SmC* phases of the sample. The observed dielectric constant and loss follow Cole-Cole behaviour in the ferroelectric phase. Various phases observed from these studies have also been identified under a cross polarizer for planar alignment of the sample. The optical transmittance data have also been taken and used to calculate the optical rotatory power for the sample.

KEYWORDS: ferroelectric liquid crystals; dielectric permittivity; relaxation frequency; optical rotatory power
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Ferroelectric liquid crystals (FLCs) have been object of extensive investigation because, apart from their potential interest in various technical applications, they possess remarkable physical and chemical properties [1]. In the last few years the properties of FLC materials with chiral Smectic C (SmC*) phase have attracted interest of the researchers due to their fast electro-optic effects [2, 3, 4], which make them promising element for optical displays. FLCs have a big advantage over nematics used in displays due to their fast optical switching response. At the same time, these materials exhibit a memory effect when placed in thin cells. This makes them potentially useful in optical switching devices [5]. Dielectric spectroscopy studies of FLCs are important as they provide useful information about the static and dynamic properties of these systems [6, 7]. The well-known relaxation modes of ferroelectric liquid crystals are Goldstone mode (GM), Soft Mode (SM) and the Polarization mode (PM).These modes

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appear due to the fluctuation of order parameter and rotation of molecule around the long molecular axis [8, 9]. FLCs in their ordered SmC* phase possess an increase in the transverse component of the dielectric constant [10]. The complex dielectric permittivity of FLCs can be obtained directly by dielectric spectroscopy techniques. With the emergence of enhanced accuracies of computer controlled bridges, it is possible to acquire dielectric permittivity and dielectric loss data rather quickly over a wide frequency range at small steps. Surface effects are also of great importance in the field of liquid crystals and the properties of FLCs are also influenced by boundary conditions. In a planar orientation, FLCs exhibit the chiral Smectic C* phase over a wide temperature range. The dielectric permittivity of a FLC can be directly measured by dielectric spectroscopic techniques. Dielectric spectroscopy data for a large number of FLCs have been reported by researchers and possible information about the molecular orientation and the relaxation time has been discussed [11, 12]. Ahuja *et al.* [13] has reported different relaxation modes and dielectric strength of some FLCs. Dielectric and optical measurement have been made on some alkoxy derivatives of 2,2-dihydroxybenzalazine by Jubindo *et al.* [14]. Dielectric studies of different thin-layered ferroelectric liquid crystals have been reported by Srivastava *et al.* [15] in different DC fields. Apart from studies on pure FLCs, many researchers are working on dye-doped, nanoparticle-doped and polymer-doped FLCs [16, 17, 18, 19, 20, 21].

The optical transmittance measurement method has been used to determine the transition temperature by many researchers, since optical transmittance is probably one of the most accurate and precise method to obtain the information about the transition temperature. The optical rotation measurements of FLCs are also important from the technical point of view as they provide information about tilt angle, *etc*. Some workers have reported temperature dependence and dispersion of the rotatory power of FLCs [22, 23].

The present paper reports the dielectric constant (ε') and dielectric loss (ε") of ZLI-3654 in the frequency range of 100 Hz to 10 MHz in a planar aligned cell. Optical rotatory power has also been reported for the planar aligned sample in the temperature range of 30°C to 62°C.

Materials and methods

The FLC material used in present investigation is ZLI-3654. The following phase transition sequence has been reported in the literature for this material:

$$Crystal \xleftrightarrow{30°C} SmC^* \xleftrightarrow{62°C} SmA \xleftrightarrow{76°C} N^* \xleftrightarrow{86°C} I$$

The sample has been placed between two glass plates (ITO coated) having a layer of polyamide aligner (Nylon 6/6) for homogeneous alignment. The sample was introduced into the cell by capillary action method in the isotropic phase and then cooled down very slowly at the rate of 0.5°C/min to make proper alignment of the molecules in the cell. Values of capacitance and dissipation factor of the sample holder with and without the sample are read from the monitor of impedance /gain phase analyser (Hewlett-Packard HP 4194-A). The formula for dielectric measurement has been published elsewhere [24]. Constant temperature was maintained using a temperature regulator (Julabo F-25).

A similar sample holder was used for the optical transmittance measurement. Here, the filled sample holder was kept over a hot stage made of a brass jacket connected to the temperature controller and the whole system was placed on the stage of a polarizing microscope. The intensity of light coming out from the eyepiece through sample was measured in the crossed and parallel conditions of the polarizers. This has been done by placing a suitable electro-optic sensor on the eye-piece [25, 26].

The optical rotatory power (ORP) was calculated using the method described by Etxebarria *et al.*, Muševič *et al.* and Shtykov *et al.* [22, 23, 27].

Results and discussion

Figure 1 shows the variation of dielectric permittivity as a function of log of frequency at two different temperatures. It is interesting to note that in the lower region of frequency the dielectric permittivity decreases sharply [28] and the nature of the variation remains almost independent of the temperature, albeit with slight decrease in its numerical value. The observed variation of dielectric permittivity for ZLI-3654 is almost similar to that of ordinary liquids [29], and is consistently decreasing with increase in frequency and become constant at higher frequencies. The dielectric constant of all the dielectrics decreases with increase in frequency as frequency increases different polarization mechanisms cease, hence dielectric constant decreases. This behaviour is almost same to that reported by other studies [30, 31] including our own [16, 17, 18].

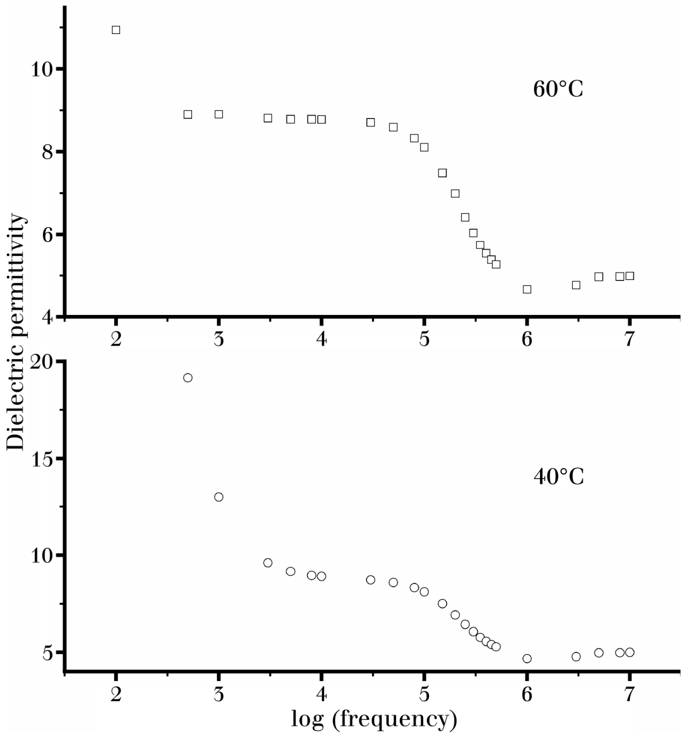

Figure 1. Variations in dielectric permittivity with the log of frequency (Hz) at 60°C and 40°C

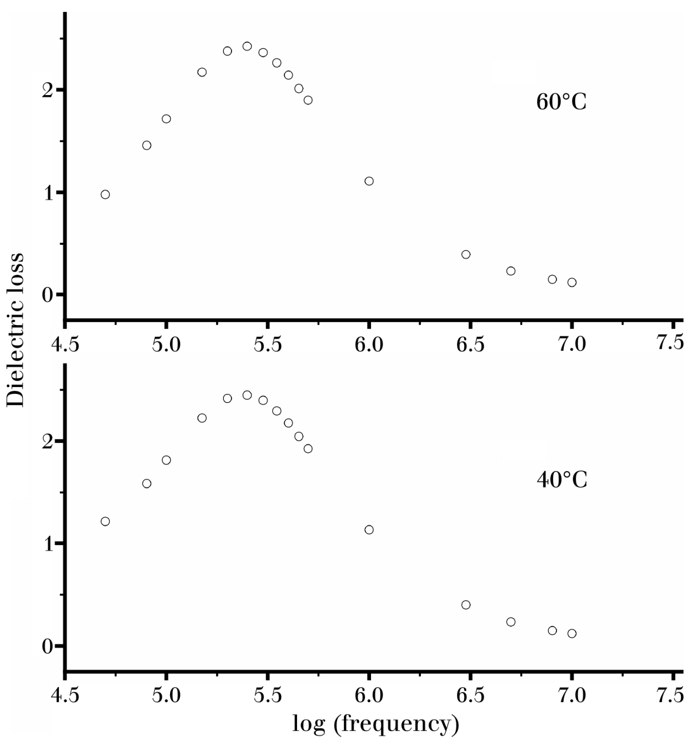

Figure 2. Variations in dielectric loss with the log of frequency (Hz) at 60°C and 40°C

Figure 2 shows a typical graph of dielectric loss against log of frequency at two different temperatures. The dielectric loss initially increases

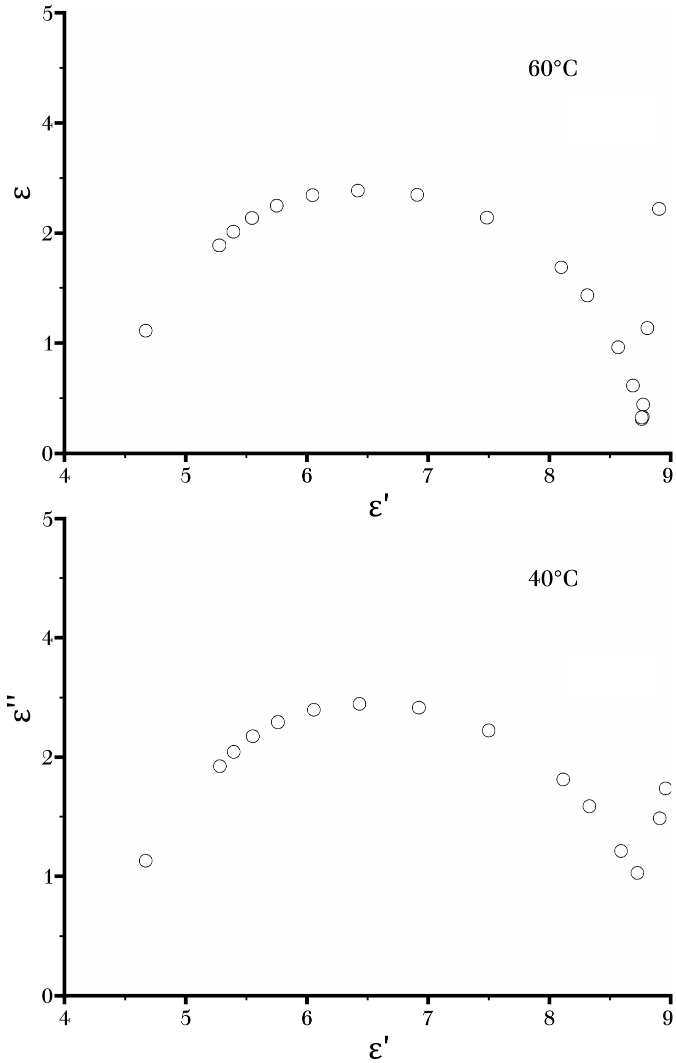

Figure 3. Representative Cole-Cole plots at at 60°C and 40°C

with the frequency and reaches a peak at 244.41 kHz and 60°C. It then decreases and become almost constant after the frequency of about 3 MHz. The dielectric relaxation frequency peak of ZLI-3654 corresponds to maximum loss. The peak value of the loss decreases with increasing temperatures. The peak position is weakly temperature dependent and shifts towards the higher frequency side with an increase in the temperature. The relaxation mode observed here may be assigned to Soft mode (SM) since the relaxation frequency is quite high (≈240 kHz). The soft mode appears near SmC*-SmA phase transition temperature due to the tilt angle fluctuation as near T_{C^*-A} the system becomes soft against these fluctuations. This mechanism is usually observed for frequencies greater than 10 kHz with strong temperature dependence [9, 32]. The Goldstone mode (GM) which is normally observed in the lower frequency range (almost from 1 Hz to 1 kHz), has not be detected in the present case as the cell is not workable in lower frequency range due to its high sheet resistance.

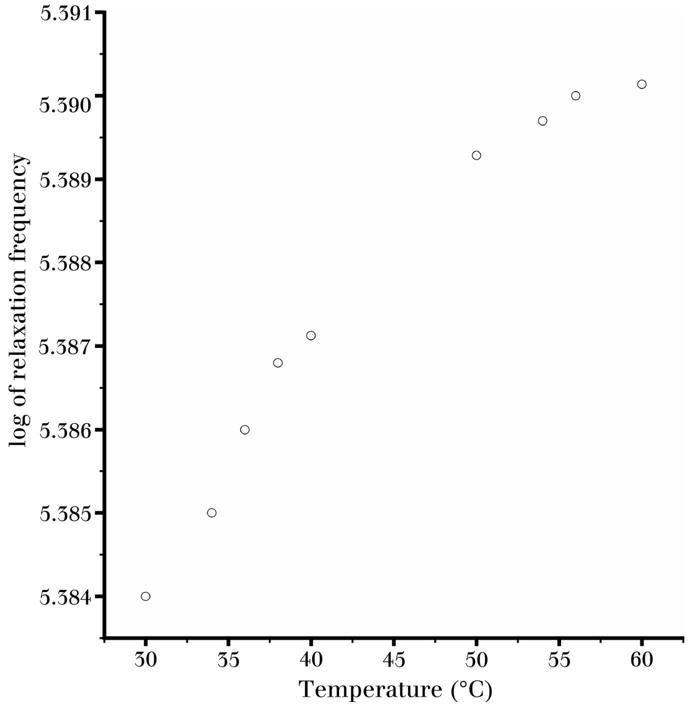

Figure 4. Relaxation frequency (Hz; f_r) as a function of temperature

It is interesting to investigate the relaxation phenomenon by Cole-Cole plot, shown in **figure 3**. The points lie almost on the semicircle except some of those at lower frequencies. The static dielectric constant ε_0 almost corresponds to the frequency 5 kHz and ε_∞ to 1 MHz approximately. The ε_∞ values were not found to be exactly same for all temperatures, perhaps because of two reasons. Firstly, due to the possibility of a second dispersion at high frequency region and secondly the estimation of ε_∞ may not be correct. The portion of the plot that can be fitted with the semicircle corresponds to the Debye relaxation. In addition to this, a relatively strong tail of low frequency can be seen. This behavior has also been observed by other workers [13, 33]. This can be explained by the energy dissipation accompanying the frequency realignment of the ferroelectric liquid crystal director at low applied frequencies, when the FLC molecules are capable of following its instantaneous value [34].

Figure 4 shows the plot of log of relaxation frequency against temperature. From the curve we find that relaxation frequency is not independent of the temperature. On heating the sample from 40°C to 60°C its value increases from 243.9 kHz to 244.41 kHz. A similar type of behavior has been observed in other studiess [11, 15]. The soft mode relaxation process is thus showing the temperature variation in which the relaxation frequency first increases with temperature and then it decreases after $T_{C^*\text{-}A}$.

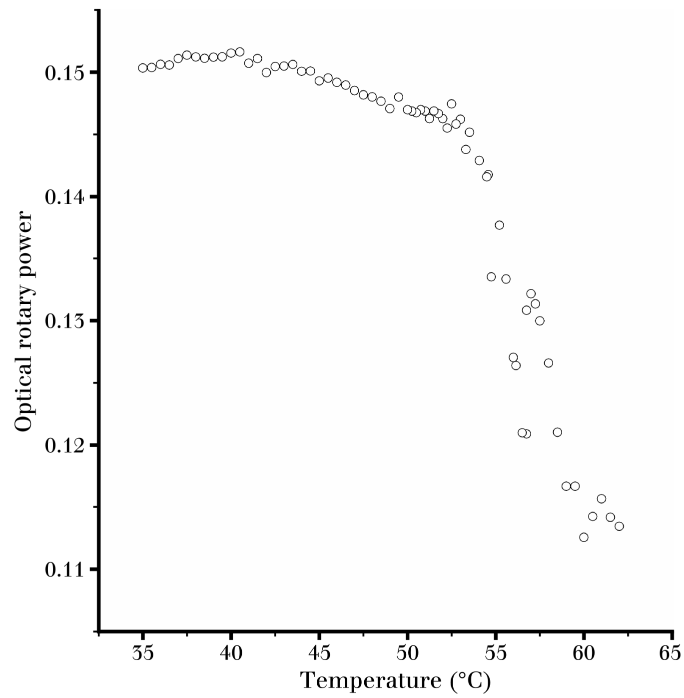

Figure 5. Variation of ORP (deg μm^{-1}) with temperature in the SmC* phase

The optical rotatory power (ORP) for chiral SmC* phase have been calculated from data of optical transmittance with and without the cross polarizer position. The ORP has been plotted against temperature in **figure 5**. The rotatory power monotonously increases with decreasing temperature. This variation of rotatory power matches well with earlier results of Musevic *et al.* [23]. As the temperature of the sample increases the helix of the sample unwinds, hence its rotatory power decreases with increase in temperature. Since we have not measured optical rotatory power with variation of wavelength, pitch of the sample cannot be calculated in SmC* phase.

Conclusion

1. Dielectric relaxation studies have been carried out in the FLC mixture ZLI-3654. The relaxation mode observed has been assigned to soft mode.
2. The dielectric response of the sample shows Cole-Cole behavior. The relaxation time (t) and thermo-dynamical parameters (ΔG_ε, ΔS_ε and ΔH_ε) have been calculated.
3. Relaxation frequency was found to be dependent on temperature as expected.
4. Optical rotatory power has been determined in the SmC* phase and the transition temperature obtained are similar to the values obtained by the dielectric measurement.

References

1. Meier, G., Sackmann, E. S., and Gragmaier, D. G. (1975) *Applications of liquid crystals*. Spinger-Verlag.
2. Ghosh, S., Nayek, P., Roy, S. K., Gangopadhyay, R., Molla, M. R., and Majumder, T. P. (2011) *Effect of conducting polymer poly (3,4- ethylenedioxythiophene) (PEDOT) nanotubes on electro-optical and dielectric properties of a ferroelectric liquid crystal*. Eur. Phys. J. E. 34: 35-40.
3. Hemine, J., Daoudi, A., Legrand, C., Elkaaouachi, A., Nafidi, A., Ismaili, M., Isaert, N., Nguyen, H. T. (2010) *Electro-optic and dynamic studies of biphenyl benzoate ferroelectric liquid crystals*. Physica B 405: 2151–2156.
4. Roy, S. S., Majumder, T. P., and Roy S. K. (1997) *Soft mode dielectric relaxation under the influence of bias electric field of a ferroelectric liquid crystal mixture*. 304(1): 315-320.
5. Clark, N. A. and Lagerwall, S. T. (1980) *Submicrosecond bistable electro-optic switching in liquid crystals*. Appl. Phys. Lett. 36 (11): 899-901.
6. Beresnev, L. A., Blinov, L. M., Osipov, M. A. and Pikin, S. A. (1988) *Ferroelectric Liquid Crystals*. Mol. Cryst. Liq. Cryst., 158(1):1-150.
7. Gouda, F., Anderson, G., Matuzezyk, M., Skarp, K. and Lagerwall, S. T. (1990) *Dielectric anisotropy and dielectric torque in ferroelectric liquid crystals and their importance for electro-optic device performance*. J. Appl. Phys. 67(1): 180-186.
8. Levstik, A., Carlsson, T., Filipic, C., Levstik, T. and Zeks, B. (1987) *Goldstone mode and soft mode at the smectic-A–smectic-C^* phase transition studied by dielectric relaxation*. Phys. Rev. A 35 (8): 3527-3534.
9. Carlsson, T., Zeks, B., Levstik, A., Filipic, C., Levstik, I. and Blinc, R. (1987) *Generalized Landau model of ferroelectric liquid-crystals*. Phys. Rev. A 36(3):1484-1487.
10. Yoshino, K., Uemoto, T., Inuishi, Y. (1977) *Ferroelectric behaviour of smectic liquid crystal*. Jap. J. Appl. Phys. 16: 571-574.
11. Biradar, A. M., Wrobel, S. and Haase, W. (1989) *Dielectric relaxation in the smectic A* and C* phases of a ferroelectric liquid crystal*. Phys. Rev. A, 39: 2693-2702.
12. Gouda, F., Skarp, K. and Lagerwall, S. T. (1989) *Proceedings 2nd international conference on ferroelectric liquid crystals*. Goteborg.
13. Ahuja, J. K., Gathania, A. K. and Raina, K. K. (2001) *Dielectric relaxation modes in ferroelectric liquid crystal mixtures*. Mol. Cryst. Liq. Cryst. 366: 271-281.
14. Jubindo, M. A. P., Ezcurra, A., Etxebarria, J., Remón, A., Tello, M. J., Marcos, M. and Serrano, J. L. (1988) *Dielectric and optical measurements for some compounds exhibiting an Is-Ch-SmC* phase transition sequence*. Mol. Cryst. Liq. Cryst. Inc. Nonlinear Opt. 159(1): 137-149.
15. Srivastava, S. L., Agrawal, V. K., Loseva, M. V., Chernova, N. I. and Beresnev, L. A. (1992) *Dielectric studies of different phases of a thin-layered ferroelectric liquid crystal with a small pitch and high spontaneous polarization*. Liq. Cryst., 11(6): 851-864.
16. Manohar, R., Yadav, S. P., Pandey, K. K., Srivastava, A. K. and Misra, A. K. (2011) *Comparative study of dielectric and electro-optical properties of pure and polymer ferroelectric liquid crystal composites*. J. Polym. Res. 18:435–441.
17. Manohar, R., Srivastava, A. K., Tripathi, P. K., Singh, D. P. (2011) *Dielectric and electro-optical study of ZnO nano rods doped ferroelectric liquid crystals*. J. Mater. Sci. 46:5969–5976.
18. Manohar, R., Yadav, S. P., Srivastava, A. K., Misra, A. K., Pandey, K. K., Sharma, P. K. and Pandey, A. C. (2009) *Zinc Oxide (1% Cu) nanoparticle in nematic liquid crystal: Dielectric and electro-optical sudy*. Jpn. J. Appl. Phys. 48: 101501-6.
19. Manohar, R., Pandey, K. K., Yadav, S. P., Srivastava, A. K. and Misra, A. K. (2010) *Surface anchoring effect on guest-host ferroelectric liquid crystal response time - an electro-optical investigation*. Philosophical Magazine, 90(34): 4529-4539.
20. Feng, Y. and Ling, Z. (2008) *Effect of dichroic azo-dye doped on ferroelectric liquid crystals*. Chin. Opt. Lett. 6(11): 858-860.
21. Srivastava, A. K., Manohar, R., Shukla, J. P. and Biradar, A. M. (2007) *Dielectric relaxation of dye-doped ferroelectric liquid crystal mixture: A comparative study of smectic C^* and smectic A phase*. Jpn. J. Appl. Phys. 46(3A): 1100–1105.
22. Etxebarria, J., Zubia, J., Remon, A. and Tello, M. J., (1989) *Temperature dependence and dispersion of the rotatory power of a ferroelectric liquid crystal in the S_I* Phase. Mol.* Cryst. Liq. Cryst. 177 (1): 35-42.
23. Muševič, I., Drevenšek, I., Blinc, R., Kumar, S. and Doane, J. W. (1989) *Temperature dependence of molecular tilt angle and rotatory power in a ferroelectric liquid crystal with polarization sign reversal*. Mol. Cryst. Liq. Cryst. Inc. Nonlinear Opt. 172: 217-222.
24. Manohar, R., Manohar, S., Chandel, V. S. (2011) *Dielectric behaviour of pure and dye-doped nematic liquid crystal BKS/B07*. Mat. Sci. and App. 2: 839-847.
25. Manohar, R., Pal, D., Shashwati, Chandel, V. S. , Mazumdar, Z. U., Paul, M. K. and Rao, N. V. S. (2012) *Dielectric and optical behavior of two calamitic hydrogen-bonded mesogens*. Mol. Cryst. Liq. Cryst. 552(1): 71-82.
26. Chandel, V. S., Manohar, R. and Shukla, J. P. (2011) *Refractive indices, order parameter and density study of BKS/B07 nematic liquid crystal*. Analele Universităţii din Bucureşti – Chimie (serie nouă), 20(02):155–163.
27. Shtykov, N. M., Vij, J. K. and Nguyen, H. T. (2001) *Optical rotatory power of different phases of an antiferroelectric liquid crystal and implications for models of structure*. Phys. Rev. E 63:051708-7.
28. Raina, K. K., Gathania, A. K. and Singh, B. (1999) *Observation of relaxation modes in room temperature ferroelectric liquid crystal mixtures*. Pramana - J. Phys. 52(4):, 443-451.
29. Hill, N. E., Vaughan, W. E., Price, A.H. and Davies, M. (1969) *Dielectric properties and molecular behavior*. V N R Compony, London.