CHAPTER-8

Summary and conclusion

The main objective of this dissertation was to characterise the phase behaviour and study the dielectric, electro-optic, structural properties of a few selected chiral liquid crystal compounds of the same homologous series (1F3R, 2F3R, 3F3R, 4F4R, 4F5R, 5F3R, 6F3R, 7F3R), with biphenyl benzoate core and fluorinated chains, whose molecular structure differ only by the number of carbon atoms and the number of oligomethylene spacers in the fluorinated chain. It was also proposed to explore a relationship of their physical properties with change in their molecular structures. Finally, it was proposed to formulate one multi-component mixture using one of the above compounds as a dopant.

In the last five chapters we have discussed in detail the characterisation of phases present in all these compounds and their structural, dielectric and electro-optic properties. In the last chapter we have also presented method of formulation and characterization of a room temperature ferroelectric liquid crystal mixture by doping the longest chain compound 7F3R in an achiral multi-component host matrix. In this chapter the major observations made in this dissertation and few insights on the structure-property correlations will be highlighted.

Analysis of the optimised molecular structures reveals:

- In three oligomithylene spacer containing compounds (nF3R), both dipole moment and optimised length are found to increase with increasing number of fluorinated carbons, except at the transition from 2F3R to 3F3R, where trend is opposite. This has been depicted schematically in the **figure 8.1**. This is because after addition of the third carbon, the fluorinated chain gets twisted in the z direction (perpendicular to the plane of molecule) by almost 87^{o}. Although in the remaining compounds it persists, but the dipole moment and molecular length continue to increase due to the addition of further carbon atoms.

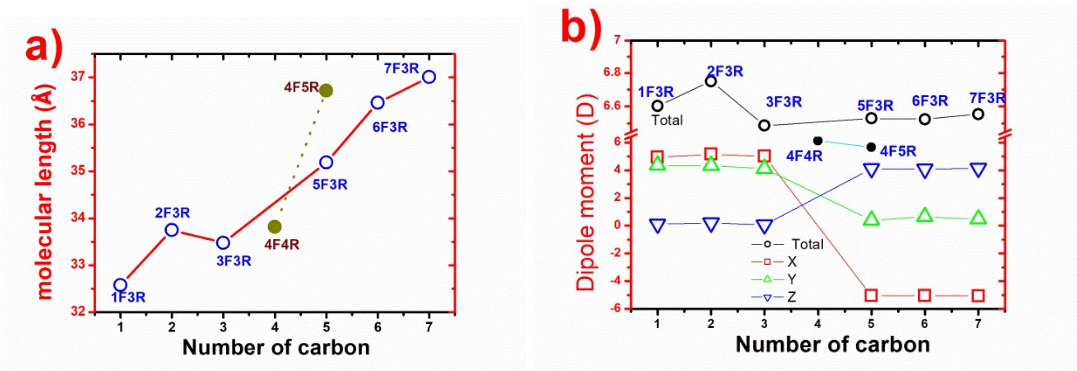

Figure 8.1: a) Optimised molecular length and b) Dipole moments of compounds nFmR. For 4F4R and 4F5R, number of oligomethylene spacers is plotted along x-axis.

- In all molecules dipole moments are found to be transverse.
- X and Y components of dipole moments change orientation with respect to the Z component from 5F3R. This might be due to a combined effect of the twist in the chain and the addition of extra 4 fluorinated carbon atoms. However, only change in sign of the Y component dipole moment of 4F5R is observed compared to 4F4R.
- The molecular length increases after addition of oligomethylene spacers (4F4R, 4F5R) as expected. However dipole moment decreases compared to nF3R series.
- Conformation of 4F5R is substantially different from other molecules. In 3F3R, 5F3R, 6F3R and even in 4F4R both the chiral chain and the fluorinated chain are bent in the same direction of the core while in 4F5R they are bent in the opposite directions.

A wide variety of orthogonal and tilted phases have been observed, at-a-glance-view of which is presented in **table 8.1**. From studying the phase sequence of the compounds it is observed:

- The compound 1F3R, having just one carbon atom in the fluorinated chain, exhibits three orthogonal smectic phases - SmE*, SmB* and SmA*. When just one extra carbon atom is added in the fluorinated chain, in 2F3R along with SmA* phase three tilted phases are induced – SmJ*, SmF* and SmC*. In the next higher homologue (3F3R) phase sequence remain same, but SmA* phase disappeared and tilting of the molecules only in the soft crystalline phase (SmJ*) changes from edge towards an apex in the pseudo-hexagonal cell giving rise to SmG* phase. Therefore, change of tilt occurs within two consecutive phases in 2F3R whereas no such change takes place in 3F3R.

Table 8.1: Phase sequence of the compounds.

Compound	Phase sequence with transition temperatures (^{o}C)
1F3R	Crystal 80 SmE* 103 $SmB_{hex}^{*\,mo}$ 121^{o}C $SmB_{hex}^{*\,lo}$ 127.5 SmA* 151 Iso
2F3R	Crystal 68 SmJ* 83 SmF* 85 (SmF*+SmC*) 100 SmC* 129 SmA*135 Iso
3F3R	Crystal 65 SmG* 73.5 SmF* 75 (SmF*+SmC*) 83 SmC* 131 Iso
5F3R	Crystal 83 SmC* 139.5 Iso
6F3R	Crystal 83 SmC* 146.2 Iso
4F4R	Crystal 86.5 SmX* 98 SmC* 130.9 Iso
4F5R	Crystal 78 SmC* 132.5 Iso
7F3R	Crystal: 75.5 SmC* 148.0 SmA* 150.1 Iso
Mixture	15 < SmC* 74.3 SmA* 101.4 Iso

- Hexagonal phases are observed only in 1F3R (orthogonal), 2F3R (tilted) and 3F3R (tilted), but not in higher homologous.

- Ferroelectric SmC* phase is observed in all except in 1F3R. Stability or thermal range of SmC* phase increases with fluorinated chain length and also with increasing oligomethylene spacers. Lower stability in 4F4R compared to 3F3R is may be due to the presence of a *subphase* (SmX*). This is depicted graphically in **figure 8.2**.

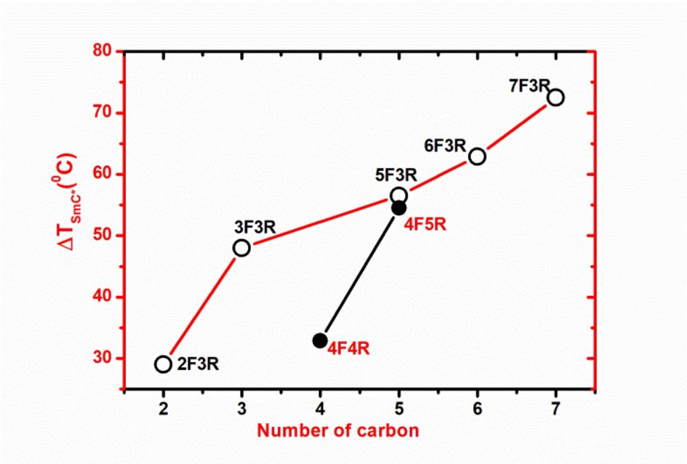

Figure 8.2: Span of SmC* phase of different compounds. For 4F4R and 4F5R, number of oligomethylene spacers is plotted along x-axis.

- In 4F4R one *subphase* is observed below SmC*. Although this phase shows many characteristics of ferrielectric SmC^*_γ phase, but since the GM dielectric increment is found to be higher than in SmC* phase, the new phase is termed as SmX* phase.
- Paraelectric SmA* phase is observed in 1F3R and 2F3R, then it is found to be absent in the higher homologous. However, it reappears in the phase sequence in the longest chain compound 7F3R. A major change in the conformations of the optimised molecular structures and thus in the dipole moments is observed from 3F3R. This results in a change in the intermolecular interactions and probably plays an important role in the

disappearance of SmA* phase. This effect is neutralized when chain length increases substantially (7F3R) and reappearance of SmA* takes place. It may further be added that even a subtle change in the intermolecular interactions produces a significant change in the phase behaviour of these kinds of self organized soft materials.

Temperature evolution of frequency domain dielectric spectroscopy gives considerable insight into the dynamics of the molecules within different phases.

- Only in the SmB* phase of 1F3R short axis flip-flop mode of molecular relaxation is observed.
- Both bond orientation order (BOO) phason and tilt phason relaxation modes are observed in the SmF* phase. This is observed in both 2F3R and 3F3R which exhibit this phase. To the best of our knowledge for the first time both (BOO) phason and tilt phason are observed in a single compound.
- Maxwell-Wagner mode of relaxation is observed only in 1F3R, 2F3R, 3F3R and 6F3R. Since MW mode is related with the accumulation of charge in the interface of heterogeneous materials, thus its presence in certain compounds and absence in others might be related with the purity of the samples.
- Goldstone mode is observed in SmC* phase of all compounds. Temperature dependences of its critical frequency and dielectric increment are explained in the light of generalized Landau theory.
- Soft mode relaxation is observed only compounds having both SmA* and SmC* phases. Thus SM is observed only in 2F3R and 7F3R (also in the mixture) throughout the SmA* phase and also in SmC* phase but in the vicinity of SmC*-SmA* transition.

- Soft mode relaxation is not observed in any other compounds, neither in SmC* phase (3F3R, 4F4R, 4F5R, 5F3R and 6F3R) nor in SmA* phase (1F3R). When a material is cooled down from orthogonal SmA* phase to the tilted SmC* phase, the elastic constant, responsible for keeping the molecules perpendicular to the smectic layer, softens considerably. Due to softening of the restoring force, when an AC signal is applied, the molecules vibrate by making their tilt angles fluctuate. This gives rise to the soft mode relaxation. Thus it is hypothesized that soft mode relaxation cannot be observed in any substance where SmA*-SmC* phase transition is absent.
- In nF3R series of compounds Goldstone mode critical frequency is found to increase with fluorinated chain length. Thus it shows a direct correlation with the dipole moments of the molecules. GM critical frequency also found to increase with increasing oligomethylene spacers. Dielectric increment also increases with chain length in these compounds with two exceptions. $\Delta\varepsilon$ of 3F3R is found to be marginally less than that of 2F3R, which may be due to smaller moment of 3F3R. $\Delta\varepsilon$ decreases sharply in the longest chain compound 7F3R becoming the least of all the compounds. $\Delta\varepsilon$ is the highest in 4F4R but decreasing once again in 4F5R. However, dipole moment of 4F5R is less than 4F4R. Thus there is also a direct correlation between the dielectric increments and dipole moments of the molecules, only exception being 7F3R These correlations are shown in **figure 8.3**.

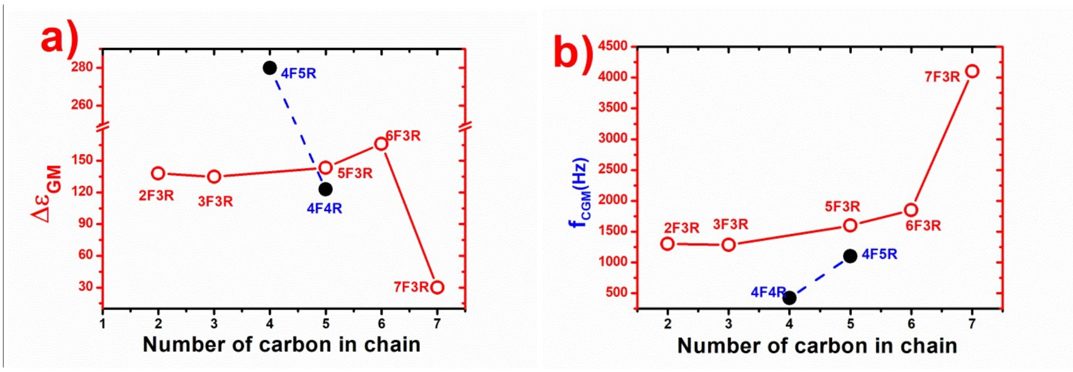

Figure 8.3: Variation of Goldstone mode a) dielectric increment (Δε) and b) critical frequency (f_C) of nFmR. For 4F4R and 4F5R, number of oligomethylene spacers is plotted along x-axis.

Structures of several higher order smectic phases of 1F3R, 2F3R, 3F3R are confirmed by synchrotron X-ray diffraction studies. Notable observations are as follows:

- The existence of two variants of SmB* phase has been confirmed in 1F3R. Cell parameters of these two phases along with of SmE* phase have been determined. Existence of a pseudo-hexagonal lattice with herringbone structure is confirmed in these phases.
- All the orthogonal phases of 1F3R are found to be partially bilayer type, which is observed, to the best of our knowledge, first time in a chiral system.
- The existence of tilted hexagonal SmF* phase has been confirmed in 2F3R and 3F3R. On further cooling soft crystal like hexagonal SmJ* phase is formed in 2F3R, undergoing a change in the tilt direction, but in 3F3R, SmG* phase is formed without any change in tilt direction. A coexistence phase of (SmC*+SmF*) is also observed in a certain temperature range in both the compounds. Cell parameters of SmF*, SmJ* and SmG* phases in 2F3R and 3F3R have also been determined.

- The SmA* phase of 2F3R and 7F3R is found to have de Vries type characteristics. Negative thermal expansion is also observed in these compounds in SmC* phase which signify possibility of reduced chevron defects in display.
- The ratio of the layer spacing (d) to the optimised molecular length (*l*) in SmA* phase is found to be the highest in the shortest chain compound 1F3R (1.07) and lowest in the longest chain one 7F3R (0.88) indicating a clear decreasing trend with increasing fluorinated chain length.

From the electro-optic response of the compounds the following observations are worth noting:

- In compounds with three oligomethylene spacers (nF3R) the highest value of spontaneous polarisation (P_S) in SmC* phase is found to increase with increasing fluorinated chain length, schematically shown in **figure 8.4**. With the addition of another oligomethylene spacer also it is found to increase and it attains the highest value in 4F5R.

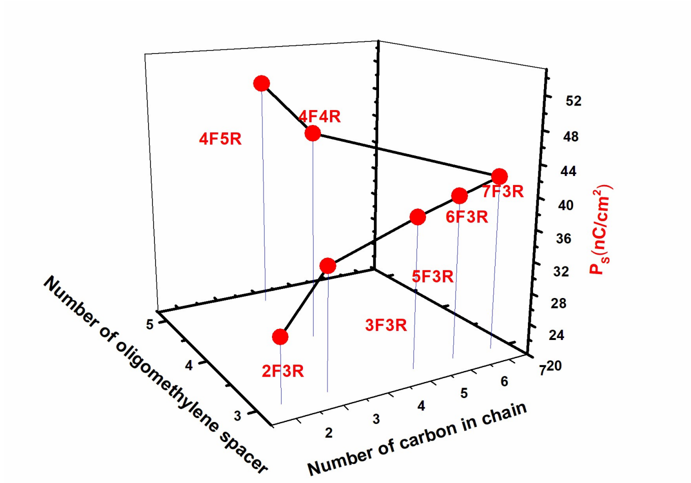

Figure 8.4: Highest value of spontaneous polarization of all compounds having SmC* phase.

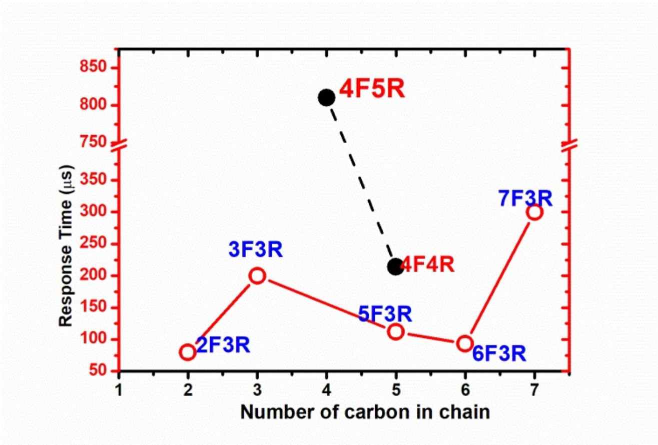

Figure 8.5: Highest value of response time of compounds nFmR. For 4F4R and 4F5R, number of oligomethylene spacers is plotted along x-axis.

- Response time (τ), the most significant parameter for display applications, is found to be the minimum in 2F3R meaning it shows fastest response to a square pulse. It is highest in 7F3R but increases further in compounds with more oligomethylene spacers which is schematically shown in **figure 8.5**. Rotational viscosity is also found to vary in a similar fashion. From these observations it may be inferred that both flexibility and dipole moment of the molecules play important role in their response to electric field

A few important selected parameters of the compounds have been gathered in **table 8.2** for ease of comparison.

Table 8.2: Few selected parameters of the compounds.

Compound	**ΔT_C* (°C)**	**Dipole moment (D)**	**Optimised molecular length (Å)**	**$\Delta\varepsilon_{GM}$**	**f_{CGM} (Hz)**	**Rotational viscosity (Pas)**	**P_S (nC/cm^2)**	**Response time (µs)**
1F3R	....	6.60	32.58	…..	…..	…..	…..	…..
2F3R	29.0	6.75	33.75	140	1300	0.05	28.0	80
3F3R	48.0	6.48	33.48	135	1285	0.28	35.0	200
4F4R	32.9	6.12	33.82	280	420	0.26	46.5	810
4F5R	54.5	5.65	36.72	123	1100	0.51	50.7	214
5F3R	56.5	6.53	35.19	143	1600	0.50	39.0	112
6F3R	62.9	6.52	36.46	166	1850	0.44	40.5	93
7F3R	72.5	6.55	37.01	30	4100	0.34	42.1	300

Finally by doping 7F3R, having highest thermal range of SmC* phase, in a four-component achiral pyrimidine based host matrix a ferroelectric liquid crystal mixture has been formulated, the following characteristics of which are worth mentioning:

- While the dopant exhibits ferroelectric SmC* phase at as high as 75.5°C, in the mixture it is induced from below room temperature and the phase is found to exist over a wide temperature range.
- The mixture also shows SmA* phase which is found to exhibit partial de Vries type characteristics and electroclinic effect.
- In the low temperature region of SmC* phase the layer spacing of the mixture is in between the host and the dopant while the tilt is found to be much higher in the mixture than in the host and the dopant.
- At room temperature moderate value of spontaneous polarization, tilt of around 20° and a response time of a few hundred microseconds make the mixture suitable to use in SSFLCDs. It is expected that problem of chevron defect and hence reduced contrast ratio problem will be minimum since the highest layer shrinkage in the SmC* phase is 3%.

APPENDIX A

LIST OF SELECTED BOOKS AND MONOGRAPHS ON LIQUID CRYSTALS

[1] Textures of Liquid Crystals. Dierking I. Weinheim: WILEY-VCH; 2003.

[2] Ferroelectric Liquid Crystals: Principles, Properties and applications. Goodby J, Blinc R, Clark N, et al. Philadelphia: Gordon & Breach; 1991.

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[4] Relaxation Phenomena: Liquid Crystals, Magnetic Systems, Polymers, High-Tc Superconductors, Metallic Glasses. Editors Hasse W, Wróbel S. Berlin: Springer; 2003.

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APPENDIX B

LIST OF PUBLICATIONS

[1] Haldar S, Sinha D, **Goswami D**, et al. Smectic layer spacing, Average intermolecular distance and spontaneous polarization of room temperature FLC mixtures. Mol. Cryst. Liq. Cryst. 2011;547:25–32. (work not presented in this thesis)

[2] Sinha D, **Goswami D**, Mandal PK, et al. On the nature of molecular associations, static permittivity and dielectric relaxation in a uniaxial nematic liquid crystal. Mol. Cryst. Liq. Cryst. 2012;562:156–165. (work not presented in this thesis)

[3] **Goswami D**, Sinha D, Debnath A, et al. Molecular and dynamical properties of a perfluorinated liquid crystal with direct transition from ferroelectric SmC* phase to isotropic phase. J. Mol. Liq. 2013;182:95–101. (work not presented in this thesis)

[4] **Goswami D**, Debnath A, Mandal PK, et al. Effect of chain length and fluorination on the dielectric and electro-optic properties of three partially fluorinated biphenylyl benzoate rigid core based ferroelectric liquid crystals. Liq. Cryst. 2016;43:1548–1559.

[5] **Goswami D**, Mandal PK, Debnath A, et al. Maxwell Wagner and Goldstone mode relaxations in a oligomethylene spacer based ferroelectric liquid crystal. AIP Conf. Proc. 2016; 1731: 040012

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[7] **Goswami D**, Debnath A, Mandal PK, et al. Orthogonal smectic phases in a biphenylyl chiral mesogen: Polarizing microscopy, synchrotron diffraction and dielectric spectroscopy studies. J. Mol. Liq. 2018;256:29–38.

[8] **Goswami D**, Sinha D, Mandal PK. Dielectric and electro-optic characterization of a partially fluorinated ferroelectric liquid crystal. AIP Conf. proceeding 2018;1953:050012.

[9] Debnath A, **Goswami D**, Mandal PK. Formulation of electroclinic, ferroelectric and antiferroelectric liquid crystal mixtures suitable for display devices. AIP Conf. Proc. 2018. p. 020001. (work not presented in this thesis)

[10] **Goswami D**, Mandal PK, Gutowski O, et al. Phase behaviour and structural properties of two members of biphenylyl benzoate chiral mesogenic series. Liq. Cryst. 2019; 46: 2115-2126.

[11] **Goswami D**, Mandal PK, Węgłowska D. Dielectric and electro-optic properties of two biphenylyl benzoate-based ferroelectric mesogens with tilted hexagonal phases. 2019 published online ; doi: https://doi.org/10.1080/02678292.2019.1686776

LIST OF PAPERS PRESENTED IN SEMINARS AND CONFERENCES

1. Presented a paper in the national conference on Nonlinear Dynamics and its applications at Dept of Physics, Darjeeling Govt College, 26th-28th November 2013.

   Title: Dielectric spectroscopy and electro optic studies of a partially fluorinated ferroelectric liquid crystal

   Author: D. Goswami, P. K. Mandal
2. Presented paper in the ***International conference on non linear dynamics and its application*** at Dept of Physics, Darjeeling Govt College,1st – 3rd November 2014

   Title: Change in the different properties of 6CHBT liquid crystal, doped with CNT particles at different Concentration

   Author: D. Goswami, P. K. Mandal
3. Presented paper in the national conference on the ***Modern Trends in Materials Science*** at Dept of Physics, University of North Bengal, 5th -6th February 2015.

   Title: Effect of multi walled carbon nano tubes on display parameters of room temperature liquid crystal 6CHBT.

   Author: D. Goswami, P. K. Mandal

4. Presented paper in the ***National conference on new approaches of basic science towards the development of engineering and technology*** at Dept of Physics Don Bosco college of engineering and technology, Assam, 27th – 28th February 2015

   Title: Dielectric and electro-optic characterization of To newly synthesized fluorinated ferroelectric liquid crystal

Author: D. Goswami, P. K. Mandal

5. Presented paper in the regional conference titled 22nd West Bengal State Science and Technology Congress-28th February-1st march 2015 at university of northbengal.

   Title: Properties of a fluorinated ferroelectric liquid crystal

   Author: D. Goswami, P. K. Mandal

6. Presented paper in the national conference on ***Indian workshop and Symposium on Modelling, Experimentation and Simulation on complex systems***, at Haldia Institute of Technology, 5th – 07th August 2015

   Title: Investigation on electro-optic properties of three newly synthesized ferroelectric liquid crystals

   Author: D. Goswami, P. K. Mandal

7. Presented a paper in the national conference at DAESSPS, Amity university, Noida, 21st -25th December 2015

   Title: Maxwell Wagner and Goldstone mode relaxations in a oligomethylene spacer based ferroelectric liquid crystal.

   Author: D. Goswami, A. Debnath, P. K. Mandal

8. Presented a paper in the national conference at DAESSPS KIT university, Bhubaneswar, 26th – 30th Decamber 2016,

   Title: Structural and electro optic properties of a Biphenyl Benzoate based chiral liquid crystal.

   Author: D. Goswami, A. Debnath, P. K. Mandal

9. Presented a paper in the ***2ND*** ICC2017, 24th-25th November2017 at Govt. Engineering College, Bikaner.

   Title: Dielectric and electro-optic characterization of a partially fluorinated ferroelectric liquid crystal.

   Author: D. Goswami, D. Sinha, P. K. Mandal

10. Presented a paper in the national conference Optical photonics and synchrotron radiation for technological application at RRCAT Bhopal on 29th April- 7th May 2018.

    Title: Identifying a new phase and revealing the structural properties of a biphenilyl chiral liquid crystal by synchrotron diffraction study

    Author: D. Goswami, A. Debnath, P. K. Mandal

11. Presented a paper in the international conference at IEMPHYS-19 at Institute of Engeneering and Management, Kolkata, 14th -16th November 2019.

    Title: Optical polarizing microscopy and electrical response time of three ferroelectric liquid crystals having biphenyl benzoate core.

    Author: D. Goswami, A. Debnath, P. K. Mandal