

*DYNAMIC RESPONSES OF FERROELECTRIC
LIQUID CRYSTAL MIXTURES DOPED WITH
NANO MATERIALS*

*A
Thesis
Submitted for the Award
of the Degree of*

DOCTOR OF PHILOSOPHY

By

NEERAJ



*SCHOOL OF PHYSICS AND MATERIALS SCIENCE
THAPAR UNIVERSITY, PATIALA-147004, INDIA
July-2011*

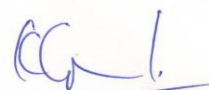


*Dedicated
To
My Family,
My Friends
&
My Guide*

CERTIFICATE

This is to certify that the thesis entitled “*DYNAMIC RESPONSES OF FERROELECTRIC LIQUID CRYSTAL MIXTURES DOPED WITH NANO MATERIALS*” which is being submitted by **Ms. Neeraj** in fulfillment of the requirement for the award of the degree of *Doctor of Philosophy* in the School of Physics and Materials Science, Thapar University Patiala, is a record of candidate's own work carried out by her under my supervision and guidance. The matter presented in this thesis has not been submitted in part or full for the award of any degree in any other University or Institute.

Date: *July 25, 2011*
Place: Patiala


Prof. K. K. Raina

Deputy Director and Distinguished Professor
School of Physics and Materials Science
Thapar University
Patiala-147004, Punjab (India)

Acknowledgement

I humbly express my deep gratitude to my research supervisor **Prof. K. K. Raina**, Deputy Director and Distinguished Professor, *School of Physics and Materials Science*, Thapar University, Patiala, for giving me the opportunity to work under his guidance and providing all the research facilities. I have been greatly benefited by his constant support, encouragement and inspiration associated with the Ph.D. work. He provided me the continuous scientific help, valuable advice, freedom of work and lots of innovative ideas which motivated me to complete my research work. It is my good fortune to work under his guidance.

My sincere thanks go to **Prof. Abhijit Mukherjee**, Director, Thapar University, Patiala, for providing the necessary infrastructure and basic facilities to carry out the experimental work in the School of Physics and Materials Science and providing opportunities for attending the various conferences, symposiums and seminars held during the term of my Ph.D.

I am greatly obliged to **Prof. O. P. Pandey**, Head, School of Physics and Materials Science, Thapar University, Patiala for his needful help during my work necessary for the successful completion of this Ph.D. research.

I express my sincere thanks to **Dr. Kulvir Singh**, Associate Professor, School of Physics and Materials Science and **Dr. Bonamali Pal**, Assistant Professor, School of Chemistry and Biochemistry, for their support in the field of research. Their constructive suggestions, motivation and constant inspiration helped me to fulfill this effort.

I am also greatly thankful to **Dr. A. M. Biradar**, Scientist G, National Physical Laboratory, New Delhi, India for allowing me to perform some experimental studies in his laboratory.

I am sincerely thankful to UGC and DRDO, New Delhi, India for the financial assistance during my work.

My special thanks go to my senior **Dr. Pankaj Kumar**, Post Doctorate Fellow, Chonbuk University, South Korea, who has greatly helped me in various stages of my research work. I will always remember his kindness and affection.

I would like to convey my sincere gratitude to my seniors and colleagues **Mr. Rakesh Kumar Sharma**, **Dr. Jitendra Kumar Kushwaha** and **Dr. Shikha Kapila**, for their co-operation.

I would love to thank all my dear friends **Ms. Pooja Sharma, Dr. Shefali Kanwar, Ms. Kamalpreet Kaur, Ms. Jasmeet Kaur, Ms. Bhupinder Kaur, Dr. Akshay Kumar, Mr. Sanjeev, Ms. Varinderjit Kaur, Ms. Anu Malik, Ms. Pratibha Singh, Dr. Zinki Jindal, Ms. Lakhvir Kaur, Ms. Mani Mahajan and Ms. Deepika Sharma** for their love and continuous encouragement. I will never forget the memorable moments spent with them.

I would like to give best wishes and thanks to my junior Ph.D. fellows **Mr. Rishi Kumar** and **Ms. Supreet** and all M. Tech./M.Sc. students who worked in the Lab for their cheerful company.

I am grateful to the all other faculty and staff of School of Physics and Materials Science who never turned me down whenever I approached them for any help. I also express my thanks and heartfelt gratitude to the other faculty and research scholars of Thapar University for their affection and co-operation.

I owe a lot to my grandmother, my parents and my sisters whose blessings and continuous encouragement have provided me strength and ability to overcome all the obstacles of my life and pursue higher studies. I also acknowledge my elders and relatives for their encouragement.

Above all, I pay my regards to the **Almighty** for his blessings.



The Author

	CONTENTS	Page No.
Certificate		i
Acknowledgement		ii
List of contents		iv
List of figures		viii
List of tables		xiv
Abbreviations and list of symbols		xv
List of publications		xvii
CHAPTER 1	General Introduction: Nano Materials Dispersed Liquid Crystals	1-44
	Overview	1
1.1	Liquid crystals	1
1.1.1	Order in liquid crystals	2
1.2	Types of liquid crystals	2
1.3	Classification of LCs composed of rod shaped molecules / calamatic liquid crystals	3
1.3.1	Nematic phase	4
1.3.2	Smectic phases	5
1.3.3	Chiral phases	8
1.4	Properties of liquid crystals	10
1.4.1	Anisotropy	10
1.4.2	Birefringence	11
1.5	Ferroelectric liquid crystals	12
1.5.1	Origin of ferroelectricity in liquid crystals	14
1.5.2	Symmetry considerations in SmC and SmC* phases	15
1.5.3	Symmetry considerations in other chiral phases	18
1.6	Ferroelectricity in other types of liquid crystals	18

1.6.1	Rod shaped molecules	18
1.6.2	Disc shaped molecules	23
1.6.3	Banana shaped molecules	25
1.6.4	Ferroelectric liquid crystal oligomers	26
1.7	Ferroelectric liquid crystal structures	27
1.7.1	Surface stabilized ferroelectric liquid crystals (SSFLCs)	27
1.7.2	Soft mode ferroelectric liquid crystal effect (SMFLC)	29
1.7.3	Deformed helix ferroelectric liquid crystals (DHFLCs)	30
1.7.4	Short pitch bi-stable ferroelectric liquid crystals (SPBFLCs)	31
1.8	Dispersed liquid crystals	32
1.9	Nano dispersed liquid crystals (nDLCs)	33
1.10	Aim of the present research and future scope	36
	References	38-44
CHAPTER 2	Theoretical Considerations For Ferroelectric Liquid Crystals	45-63
	Overview	45
2.1	Dielectric relaxations	45
2.1.1	Debye type relaxation	46
2.1.2	Non-Debye relaxation	49
2.1.3	Cole-Cole plots	51
2.2	Dielectric relaxations in low molar mass liquid crystals	52
2.2.1	Collective polarization mechanism in chiral smectic phases	52
2.2.2	Non-collective polarization mechanism	57
2.3	Theory of electro-optics	59
2.4	Transmission studies	60
	References	62

CHAPTER 3	Sample Cell Preparation and Experimental Techniques	64-82
	Overview	64
3.1	Materials used	64
3.2	Fabrication of LC cells	65
3.2.1	Liquid crystal cell alignment	65
3.2.2	Polymer rubbing and empty cell construction	68
3.3	Preparation of nano materials dispersed ferroelectric liquid crystal composites	70
3.4	Instruments used and experimental techniques	70
3.4.1	Phase identification and transition temperature studies	70
3.4.2	Dielectric studies	73
3.4.3	Polarization switching studies	77
3.4.4	Transmission studies	80
3.4.5	Tilt angle measurements	81
3.4.6	UV-VIS Spectrophotometer for absorbance studies	81
	References	82
 CHAPTER 4	 Silica nanoparticles dispersed liquid crystal composites	 83-108
	Overview	83
4.1	Introduction	83
4.3	Experimental details	84
4.4	Results and discussion	85
4.4.1	Isotropic temperature	85
4.4.2	Texture morphology	85
4.4.3	Dielectric spectra	88
4.4.4	Electro-optic studies	94
	References	106

CHAPTER 5	CNT dispersed ferroelectric liquid crystal composites	109-128
	Overview	109
5.1	Introduction	109
5.2	Carbon nano tubes	111
5.2.1	Properties based applications of CNTs	113
5.2.2	Functionalization of CNTs	113
5.3	Results and discussion	114
5.3.1	Thermo-optic studies	114
5.3.2	Switching responses in micro-textures	117
5.3.3	Dynamic responses and dielectric spectroscopy	120
5.3.4	Electro-optic studies	125
	References	126
CHAPTER 6	Nickel nanoparticles dispersed ferroelectric liquid crystal composites	129-142
	Overview	129
6.1	Introduction	129
6.2	Experimental	130
6.3	Results and discussion	133
6.3.1	Characterization of nickel nanoparticles	133
6.3.2	Transition temperature changes	133
6.3.3	Textural studies	135
6.3.4	Electro-optic studies	136
6.3.5	Opto-dielectric responses	138
6.3.6	Switching responses	140
	References	141
CHAPTER 7	Conclusions	143-144

LIST OF FIGURES

Page No.

CHAPTER 1

1.1	Molecular arrangements in (a) solid crystal (b) liquid crystal and (c) isotropic liquid.	1
1.2	Classification of liquid crystals	3
1.3	A general structure template for generating single compound calamitic LCs	4
1.4	(a) Schematic representation of the two dimensional orientation of the LC molecules, tending to align along the director, n (b) optical texture of nematic phase between crossed polarizer.	4
1.5	(a) Smectic A phase of liquid crystal. The long axes of the molecules in each layer, on an average, are perpendicular to the layer plane containing the molecules (b) optical micro texture of SmA phase.	6
1.6	Smectic C phase of liquid crystal. The long axes of the molecules in each layer are tilted at an angle with respect to layer normal	7
1.7	Structures of various smectic liquid crystal phases	7
1.8	Schematic representation of molecular structure of (a) cholesteric liquid crystal (b) optical texture of cholesteric phase	8
1.9	Modulated structure of chiral smectic C (SmC*) phase resulting in the helix formation	10
1.10	Incident light gets bifurcated into an ordinary and extra ordinary ray due to anisotropy in a birefringent material	11
1.11	Different angles made by polarization vector with the director field	11
1.12	The geometry of ferroelectric liquid crystal molecule	12
1.13	(a) Ferroelectric SmC* structure and (b) Unwound SmC* structure	14
1.14	Reduced symmetry in SmC* phase. The dipoles represented by μ are perpendicular to the plane of page and parallel to the C_2 axis (Arrows represent the dipole moment and not the vector)	16
1.15	A typical structure of a chiral, calamitic, rod-like liquid crystalline compound. Here n , m and P are integers; $(B+m)$ is the parity; A and X	19

	are polar groups; Y and Z are different substituent; * denotes a chiral centre	
1.16	General structure of chiral materials for ferroelectric mixtures	20
1.17	Structural model of comb like polymer with lateral mesogenic unit	23
1.18	A general structural template for discotic liquid crystals	24
1.19	Disc shaped molecules in (a) nematic and (b) columnar discotic liquid crystals	24
1.20	Geometry of banana shaped liquid crystal	26
1.21	Schematic surface stabilized ferroelectric SmC* liquid crystal geometry with tilt angle $\theta(T)$ and spontaneous polarization $P_s(T)$	28
1.22	Chevron layered stacking in SSFLCs	29
1.23	Schematic geometry of deformed helix ferroelectric SmC* liquid crystal	31
1.24	The short pitch bi-stable configuration	32

CHAPTER 2

2.1	The simple Debye type relaxation behaviour of real and imaginary parts of permittivity	47
2.2	Different relaxations present in the materials with a range of frequencies represented in the form of variation real and imaginary part of permittivity	50
2.3	Cole-Cole plots for a Debye dielectric relaxation	51
2.4	Cole-Cole plots showing the overlapping of modes at different temperatures for CG50 data. These are complex and show deviation from pure Debye behavior	51
2.5	Representation of (a) the polarization and tilt order parameters (b) amplitude changes connected to soft mode (c) phase changes connected to goldstone mode	54
2.6	Geometry for the maximum (a) GM contribution & (b) SM contribution	57
2.7	Component of dipole moment both parallel and perpendicular to the long axis	58

	of the molecules	
2.8	Re-orientation around the short molecular axis of the molecules	59
2.9	Output wave form obtained after applying peak to peak voltage in transmission studies	61

CHAPTER 3

3.1	Molecular structure of the main components of FLCI	65
3.2	Molecular structure of FLCII	65
3.3	Homogeneous and homeotropic alignment	67
3.4	Spin coating unit for polymer coating of glass substrates	67
3.5	Assembled empty sample cell construction	68
3.6	(a) Filled silica dispersed FLC sample cells with varying silica nanoparticles concentration	68
3.7	Flow chart for the preparation and characterization of nano dispersed ferroelectric liquid crystal composite cells	69
3.8	Block diagram of optical thermal polarizing microscopy	72
3.9	Differential scanning calorimeter	72
3.10	Block diagram of experimental set-up for dielectric measurements	73
3.11	(a) Arc plot for a Debye dielectric and (b) arc plot for a dielectric with a Cole-Cole distribution characterized by parameter α	76
3.12	Block diagram of experimental set-up used for electro-optic studies	78
3.13	(a) Triangular wave output and (b) square wave output	78
3.14	Measurement of the tilt angle θ ; typical form of electro-optical response at two extreme positions of the cone: (a) angle θ ; (b) angle $-\theta$	81

CHAPTER 4

4.1	Micro textures of 0.1% SiO ₂ -FLCI composite under crossed polarizers at 10X	86
4.2	Micro textures of the various sample cells at $\Delta T = -25^{\circ}\text{C}$	87
4.3	Micro textures of various samples at -5°C reduced temperature on cooling	87

4.4	Dielectric permittivity as a function of frequency at $\Delta T = -25^{\circ}\text{C}$	89
4.5	Dielectric permittivity as a function of reduced temperature at 100 Hz	89
4.6	Dielectric loss as a function of field frequency at $\Delta T = -25^{\circ}\text{C}$	91
4.7	Variation of (a) dielectric permittivity and (b) dielectric loss as a function of silica concentration at different bias voltage at $\Delta T = -25^{\circ}\text{C}$ and 100 Hz	92
4.8	Cole – Cole profiles of the un-doped and silica doped samples at $\Delta T = -25^{\circ}\text{C}$	93
4.9	Temperature dependence of dielectric strength of GM and SM	93
4.10	GM relaxation frequency as a function of silica concentration at 100 Hz	94
4.11	(a) Effect of temperature on polarization hump in 0.01% silica sample at 30V and (b) variation of spontaneous polarization with reduced temperature at 30V in various samples	95
4.12	Variation of tilt angle as a function of reduced temperature in various samples	97
4.13	a) Effect of voltage on polarization hump in 0.01% silica sample at -25°C (b) Variation of spontaneous polarization with applied voltage at -25°C in various samples	98
4.14	(a) Effect of voltage on switching response in 0.01% silica sample at -25°C and (b) effect of temperature on switching response at 20V in 0.01% silica sample	100
4.15	(a) Variation of response time with reduced temperature at 30V in various samples (b) Variation of rotational viscosity with reduced temperature at 30 V in various samples	101
4.16	Optical transmission as a function of applied voltage at $\Delta T = -25^{\circ}\text{C}$	103
4.17	Variation of contrast ratio with reduced temperatures in various silica samples	103
4.18	Variation of threshold voltage and driving voltage with silica concentration	104

CHAPTER 5

5.1	Structure of (a) single walled carbon nanotube and (b) multiwalled carbon nanotube	112
5.2	DSC profiles of undoped FLCII (a) and CNT doped FLCII (b, c & d) composites on heating the sample	115-116
5.3	Transition temperature variation of various phases as a function of	117

	CNT concentration on cooling the samples from their isotropic temperature	
5.4	Micro-textures of undoped and CNT doped samples in SmC* phase on cooling	117
5.5	Switching responses of 0.02 % CNT-FLC composite in presence of an electric field	118
5.6	Switching responses of various CNT-FLCII composites in presence of an electric field for green colour	119
5.7	Variation of switching voltage for green colour as a function of CNT concentration	120
5.8	Variation in the dielectric permittivity of various samples as a function of (a) frequency and (b) CNT concentration in FLC matrix ($\Delta T = -5^\circ\text{C}$)	121
5.9	Variation in the dielectric loss as a function of (a) frequency and (b) CNT concentration ($\Delta T = -5^\circ\text{C}$)	121
5.10	Variation of ac conductivity with frequency and with CNT concentration at fixed temperature (-5°C)	122
5.11	(a) Cole-Cole plots in SmC* phase and (b) variation of GM strength with reduced temperature in CNT doped samples	123
5.12	(a) Variation of GM relaxation frequency (a) with reduced temperature in various samples and (b) as a function of CNT concentration in FLCII matrix	124
5.13	(a) Variation of spontaneous polarization and (b) response time with reduced temperature in various samples at 30V	124

CHAPTER 6

6.1	Flow chart for the preparation of nickel nanoparticles	131
6.2	XRD pattern of nickel nano powder	131
6.3	TEM micrographs at (a) 120000X (b) 200000X and (c) 600000X magnifications show that particle size of nickel nano particles lies between 2-8nm	132-133
6.4	Optical textures of 0.5% Ni-FLCIII composite at (a) 87°C (b) 85°C (c) 80°C (d) 75°C (e) 66°C (f) 65°C (g) 60°C (h) 55°C (i) 30°C respectively.	134

6.5	Optical micrographs of (a) SmC* (b) SmA phases of undoped FLCIII and (c) SmC* (d) SmA phases of 0.5% Ni-FLCIII composite. Arrows show the rubbing direction.	135
6.6	(a) Optical transmission as a function of applied voltage at fixed frequency 50Hz (b) UV-Vis graph and (c) tilt angle variation with temperature in the two samples.	137
6.7	Temperature variations of (a) dielectric permittivity at different frequencies and (b) conductivity at 100Hz frequency	138
6.8	Variation of (a) spontaneous polarization and (b) response time as a function of applied voltage at room temperature (30°C) (c) relaxation frequency as a function of temperature	139

	LIST OF TABLES	Page No.
1.1	Historical overview of nano dispersed liquid crystals	33
2.1	Possible polarization mechanisms in liquid crystals	46
3.1	Phase sequences and physical properties of the various FLCs used	66
3.2	Physical properties of silica nano particles.	66
3.3	Physical properties of multi walled carbon nano tubes	66
4.1	Investigated isotropic temperature of silica doped samples	86
5.1	Phase transition temperatures of various samples on cooling	116
6.1	Transition temperature of different phases	134

ABBREVIATIONS AND LIST OF SYMBOLS

LC	Liquid crystal
FLC	Ferroelectric liquid crystal
nDFLC	nano dispersed ferroelectric liquid crystal
Cr	Crystalline
I	Isotropic
N*	Cholesteric
SmA	Smectic A
SmC	Smectic C
SmC*	Smectic C*
SSFLC	Surface-stabilized ferroelectric liquid crystal
ITO	Indium tin oxide
NOA	Norland optical adhesive
DSC	Differential scanning calorimetry
XRD	X-ray diffraction
TEM	Transmission electron microscope
CNT	Carbon nanotube
SWCNT	Single walled carbon nanotube
MWCNT	Multi walled carbon nanotube
GM	Goldstone mode
SM	Soft mode
α	Distribution parameter
T_{C^*A}	SmC* to SmA transition temperature
T_{N^*I}	Cholesteric to isotropic transition temperature
ΔT	Reduced temperature
$\Delta\epsilon$	Dielectric strength
$\delta\epsilon$	Dielectric anisotropy
I_o	Incident light intensity
I_t	Transmitted light intensity
β	Absorbance coefficient

d	Cell thickness
T	Transmittance
CR	Contrast ratio
V_{th}	Threshold voltage
V_{dr}	Driving voltage
C	Stray capacitance
ϵ'	Dielectric permittivity
ϵ''	Dielectric loss
ϵ_0	Free-space permittivity
f_r	Relaxation frequency
σ_{AC}	AC conductivity
P_s	Spontaneous polarization
τ_R	Response time
η	Rotational viscosity

LIST OF PUBLICATIONS

International Journals

1. Influence of silica nano-particles on the dielectric spectroscopy and polarization switching responses of novel ferroelectric liquid crystals, **Neeraj** and K.K. Raina, *Phase Transitions*, 2010, Vol.83, issue 8, 615-626.
2. Dynamic responses of dispersed ferroelectric liquid crystal composite systems, **Neeraj** and K.K.Raina, *Integrated Ferroelectrics*, 2011, Vol.125, 104-110.
3. Analysis of dichroic dye-doped polymer dispersed liquid crystal materials for display devices, Pankaj Kumar, **Neeraj**, Shin W Kang, Seung H Lee, Kuldeep K Raina, *Thin Solid Films*, 2011 (In Press).
4. Switching responses of ferroelectric liquid crystal mixture doped with silica nano particles, **Neeraj** and K.K.Raina, *Journal of Applied Physics (Communicated)*.
5. Effect of nickel nanoparticles on electro-optic parameters of ferroelectric liquid crystals, **Neeraj** and K.K.Raina (*Communicated*).
6. Effect of nano materials on dielectric and electro-optic responses of a novel ferroelectric liquid crystal mixture, **Neeraj** and K.K.Raina (*to be communicated shortly*).

International/National Conference Proceedings

1. Electro-optic and dielectric responses of a novel ferroelectric liquid crystal mixture dispersed with nano particles, **Neeraj** and K.K. Raina, *National Conference on Liquid Crystals (NCLC-15)*, IISC, Bangalore, 13-15 Oct, 2008.
2. Electro-optic behavior of ferroelectric liquid crystal mixture, **Neeraj**, Pankaj Kumar and K.K. Raina, *National Seminar on Ferroelectrics and Dielectrics (NSFD-15)*, Thapar University, Patiala, 6-8 Nov., 2008.
3. Effect of silica nano particles on dynamic responses of ferroelectric liquid crystal mixture, **Neeraj**, Pankaj Kumar and K.K. Raina, *Conference on Mesogenic and Ferroic Materials (CMFM09)*, BHU, Varanasi, 9-11 January, 2009.
4. Some investigations on nano dispersed liquid crystalline colloidal systems, K.K. Raina, Ravi Shukla and **Neeraj**, *National Conference on Recent Advances in Condensed Matters Physics (RACMP-2009)* NIT, Hamirpur, HP, May 23-34, 2009.

5. Effect of functionalized MWCNTs on the dielectric behaviour of a high polarization ferroelectric liquid crystal mixture, **Neeraj** and K.K. Raina, **16th National Conference on Liquid Crystals (NCLC-2009)**, University of Lucknow, Lucknow, Oct. 26-28, 2009.
6. Influence of silica nano particles and CNTs on dielectric responses of a novel ferroelectric liquid crystal mixture, **Neeraj**, Pankaj Kumar and K.K. Raina, **International Symposium on Nanostructured Materials (ISNM-09)**, Kanya Maha Vidyalaya, Jalandhar, Oct.28-29,2009.
7. Dynamic responses of dispersed ferroelectric liquid crystal composite systems, K.K. Raina and **Neeraj**, **International Symposium on Integrated Functionalities (ISIF 2010)**, University of Puerto Rico , San Juan, Puerto Rico, June 13-16, 2010.
8. Switching Responses of silica nano particle - ferroelectric liquid crystal composites for high contrast displays, **Neeraj** and K.K. Raina, **International Conference on Nano Sensors & Technology (ICNST2010)**, Central Scientific Instruments Organization (CSIO), Chandigarh, India, October 28-30, 2010.
9. Effects of nano-particle doping on the physical properties of ferroelectric liquid crystals, **Neeraj** and K.K. Raina, **International Conference on Advances in Condensed & Nano Materials, (ICACNM 2011)**, Panjab University, Chandigarh, India, February 23-26, 2011.
10. Improved electro-optic and opto-dielectric responses of Ni nanoparticles doped ferroelectric liquid crystals, K.K. Raina and **Neeraj**, **Joint International Conference the 20th IEEE International Symposium on Applications of Ferroelectrics & the International Symposium on Piezoresponse Force Microscopy & Nanoscale Phenomena in Polar Materials (ISAF-PFM-2011)**, Vancouver, BC, Canada, July 23-27, 2011.

CHAPTER 1

General Introduction:

Nano Materials

Dispersed Liquid

Crystals

Overview

This chapter reviews the basic features and classification of liquid crystals (LCs) in general and ferroelectric liquid crystals (FLCs) in particular. The various liquid crystalline phases, order parameter and LC alignments are defined, followed by the effects of molecular chirality to induce ferroelectric properties in the LC materials. The various electro-optic structures of FLCs are described in detail. This chapter also includes a brief discussion on research works already accomplished by various research groups in the area of nano dispersed LCs (nDLCs). The operation principle of nano dispersed FLC (nDFLC) systems is also given. The objectives of present research work and the future scope have been described at the end of the chapter.

1.1 LIQUID CRYSTALS

Liquid crystals are the organic compounds which were first discovered by Reintzer and Lehmann in 1888 [1-3]. They exhibit a phase of matter that has properties between those of a solid and a liquid as shown in fig.1.1. Such phases are referred as mesomorphic phases or simply liquid crystalline phases. The molecules of liquid crystals have rod-shaped structure. They exhibit rigidity along the long axis and are easily polarizable substituents. The distinguishing characteristic of the liquid crystals is to point along a common axis $\mathbf{n}$, called the *director*. This leads to a condition known as anisotropy i.e. the *properties of a material depend on the direction in which they are measured*. This nature is responsible for the unique optical properties exploited by scientists and engineers in a variety of applications [4-7].

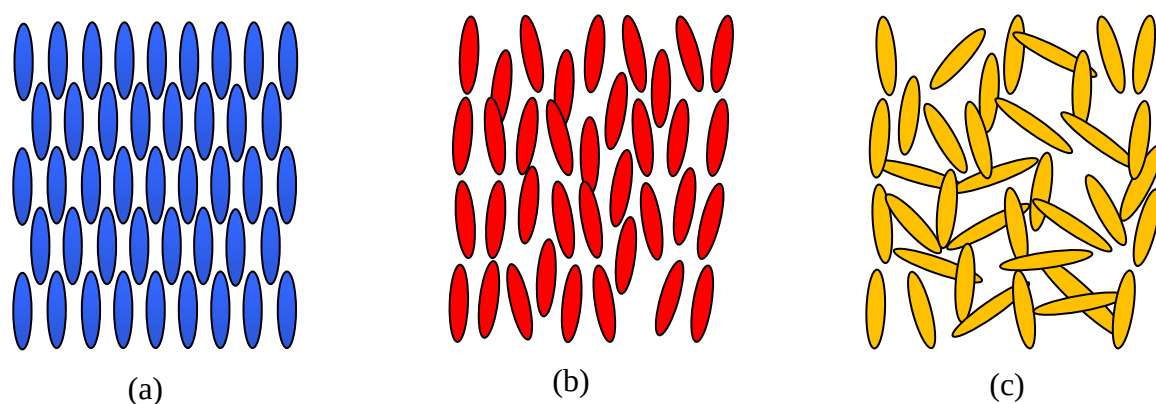


Figure 1.1 Molecular arrangements in (a) solid crystal (b) liquid crystal and (c) isotropic liquid.

1.1.1 Order in liquid crystals

The molecules in the liquid phase have no intrinsic order. In the solid state, molecules are highly ordered. The orientational order of the liquid crystal state is between a traditional solid and liquid phases. To check that how much order is present in a material, an order parameter (S) is defined as

$$S = (1/2) \langle 3\cos^2\theta - 1 \rangle \quad (1.1)$$

Here θ is the angle between the molecular axis and the director [5-8]. For isotropic liquids, $S=0$. For perfect crystals, $S=1$ and for LCs S lies between the range 0.3 to 0.9. The order parameter is a function of temperature as a result of kinetic molecular motion. Various parameters i.e. positional order, orientational order and bond orientational order describe the extent to which liquid crystal sample is ordered. Positional order describe the extent to which an average molecule or group of molecules show translational symmetry whereas orientational order represents measure of tendency of the molecules to align along the director (average direction of molecules denoted by n) on a long range basis. Bond orientational order describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line. Rod shaped molecules in smectic phase show orientational as well as translational order not present in nematics. Smectics are more ordered which means that smectic state is more ‘solid like’ than nematics. In the smectic state, molecules maintain the general orientational order of nematics, but tend to align themselves in layers or planes. The details of these liquid crystal phases are discussed in section 1.3.

1.2 TYPES OF LIQUID CRYSTALS

On the basis of their structure, phase transition, molecular shape and molecular arrangement, classification of liquid crystals is shown in fig.1.2. Liquid crystals may exist in the monomer as well as polymer form. However, based on the chemical view point, they may be broadly classified mainly into two types: *Thermotropic* and *Lyotropic* liquid crystals. Thermotropic LCs exhibit a phase transition into LC phase as the temperature is changed [9-10], whereas lyotropic LCs exhibit phase transitions as a function of concentration of the mesogen in a solvent as well as temperature. Many thermotropic LCs exhibits a variety of phases as temperature is changed. For instance, a particular mesogen may exhibit various smectic and nematic phases as the temperature is increased. In contrast to the thermotropic LCs, lyotropics have another degree of freedom

of concentration that enables them to induce a variety of different phases [10-12]. Thermotropic LCs are of interest, both from basic research point of view as well as for applications in electro-optic displays, temperature and pressure sensors etc. Lyotropic liquid crystals, on the other hand, are of great interest biologically and appear to play an important role in living systems. The molecules of thermotropic and lyotropic liquid crystals may be rod shaped (calamatic LCs), disc shaped (discotic LCs) or bent shaped (banana LCs). However, a majority of them are composed of rod shaped molecules.

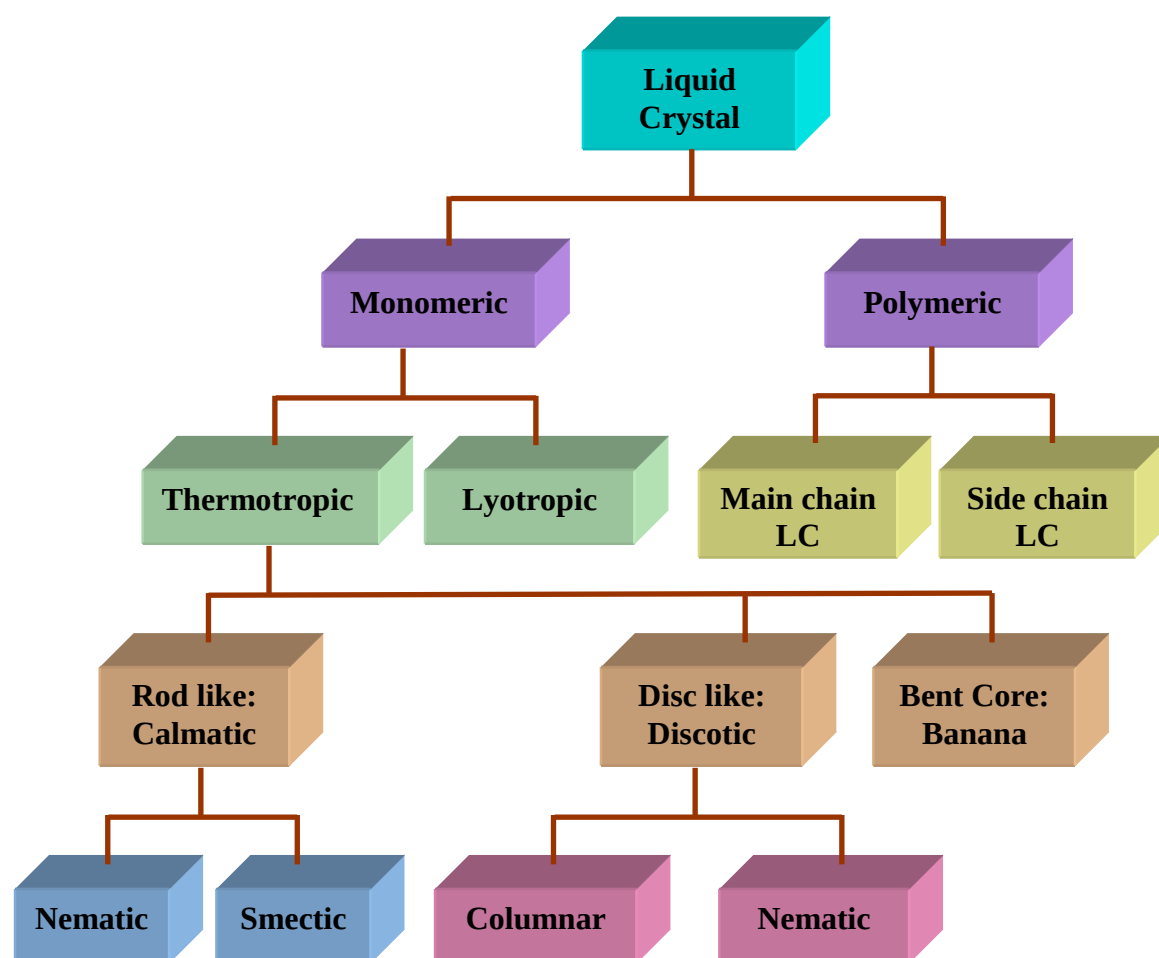


Figure 1.2 Classification of liquid crystals.

1.3 CLASSIFICATION OF LCs COMPOSED OF ROD SHAPED MOLECULES / CALAMITIC LIQUID CRYSTALS

Based on the molecular arrangement, the LCs are classified into three main categories i.e. nematics, cholesterics and smectics [9]. A compound may possess one or combination of these phases. A common feature of these phases is that their molecules comprise a central rigid core connected to a flexible alkyl chain at one or both the ends. A general

structure template for calamitic liquid crystal is shown in fig. 1.3 [4]. In calamitic LCs, one of the molecular axes is much longer than the other two. The important property for calamitic or rod like LCs is that the molecule should be rigid for at least some portion of its length, since it must maintain an elongated shape in order to produce interactions that favor alignment.

- A and B are core units, which are sometimes linked by linkage group (Y) but more often a direct link is used.
- The terminals chains (R and R') can be linked to the core, with the groups X and Z but usually the terminals chains are directly linked to the core.
- Lateral substituents (M and N) are often used to modify the mesophase.
- Morphology and physical properties of LCs to generate enhanced properties for applications.

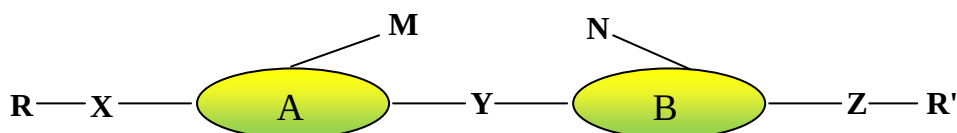


Figure 1.3 General structure template for generating single compound calamatic LCs [4].

1.3.1 Nematic phase

Nematic phase is the most common and simplest phase of liquid crystals. The name ‘nematic’ comes from a Greek word for ‘Thread’ as thread like textures were observed for this phase when viewed through the optical polarizing microscope.

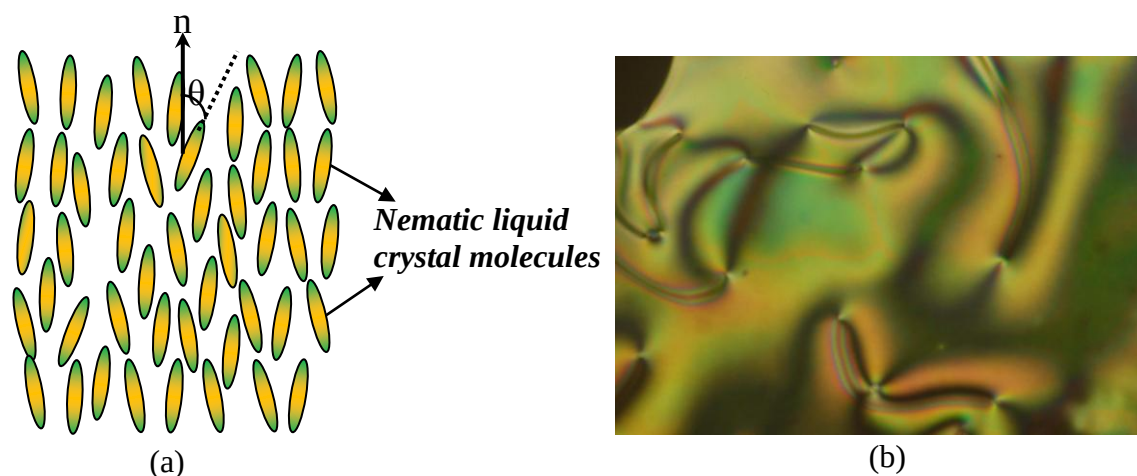


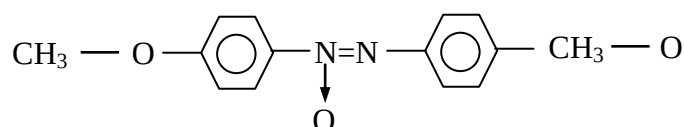
Figure 1.4(a) Schematic representation of two dimensional orientation of the LC molecules tending to align along the director, n (b) optical texture of nematic phase between crossed polarizer.

Nematics possess several main features:

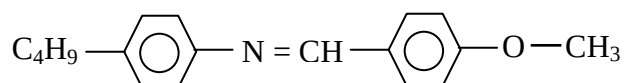
- (a) Long range orientational order i.e. the molecules tend to align parallel to each other.
- (b) Fluid-likeness, i.e., there is no long range order in the molecular center of gravity (translational order).
- (c) The states of director $\mathbf{n}$ and $-\mathbf{n}$ are equivalent. It means that director has no polarity.

A nematic molecule is not symmetrical in their structure.

Fig.1.4(a) is the schematic representation for nematics. The micro-texture of typical nematic phase is shown in fig. 1.4 (b), as the Schlieren texture. In this phase, the molecules possess a preferred direction of orientation throughout the sample, but there is no translational order [6-7]. Order parameter (S) for nematic formed by rod-like molecules is between 0.4 (at the highest temperature) and 0.7 (at the lowest temperature). Based upon their molecular structure and chemical behaviour, there are two primary types of nematics i.e. uniaxial and biaxial. The uniaxial nematic phase has bond orientational order but no positional order. It possesses orientational order parallel to the director that has arbitrary direction in the space; typically imposed by the outside forces like electric and magnetic field. The $\mathbf{n}$ and $-\mathbf{n}$ are equivalent and the molecules which form nematics are either achiral or racemic. In addition, a biaxial phase possesses two different directions perpendicular to director rendering it biaxial. It results due to further breaking of rotational symmetry of the system around the director $\mathbf{n}$. A typical example of nematic liquid crystals is p-azoxyanisole (PAA) with the chemical structure [13]:



The two benzene rings are nearly coplanar. Such a nematic molecule can be considered as a rigid rod with 20 Å in length and 5 Å in width approximately. Other classical liquid crystalline molecule is methoxy benzilidene butyl aniline (MBBA) with the chemical structure



This material has a wide room temperature nematic phase.

1.3.2 Smectic phases

The smectic word is derived from Greek word for ‘soap’. The reason behind this may be explained by the fact that the thick and slippery substance found at the bottom of a soap

dish is a type of smectic liquid crystal. Smectics is the name coined by Friedel [4-5]. The smectic phase molecules show a degree of translational order not present in the nematic phase. In the smectic phase, molecules maintain the general orientational order of nematics, but also tend to align themselves in layers or planes with a well defined interlayer spacing due to translational order that can be measured using X-ray diffraction technique. The interlayer attractions are weak as compared to lateral forces between molecules. The layers are able to slide over one another and motion is restricted within these layers or planes. This gives rise to fluidity to the system with higher viscosity than nematics which means that smectic state is more ‘solid like’ than nematic. There are many different types of smectic phases observed and each differs from the other in the way of layer formation and existing order inside the layers e.g. smectic A (SmA), smectic B (SmB), smectic C (SmC), smectic E (SmE) etc. [5]. These are given names depending upon their order of invention. Out of these, SmA and SmC are most common phase and discovered earlier.

SmA phase

In SmA phase, the average molecular axis is normal to the smectic layers and it consist of non-chiral and non-polar molecules. This phase is more ordered than nematic phase and possesses positional as well as orientational order but there is no particular positional order in the layer. The SmA phase usually occurs at a temperature below the nematic domain. The SmA phase is uniaxial with the optical axis direction coinciding with the director as seen in fig1.5 (a). Fig. 1.5 (b) shows the optical texture of the SmA phase.

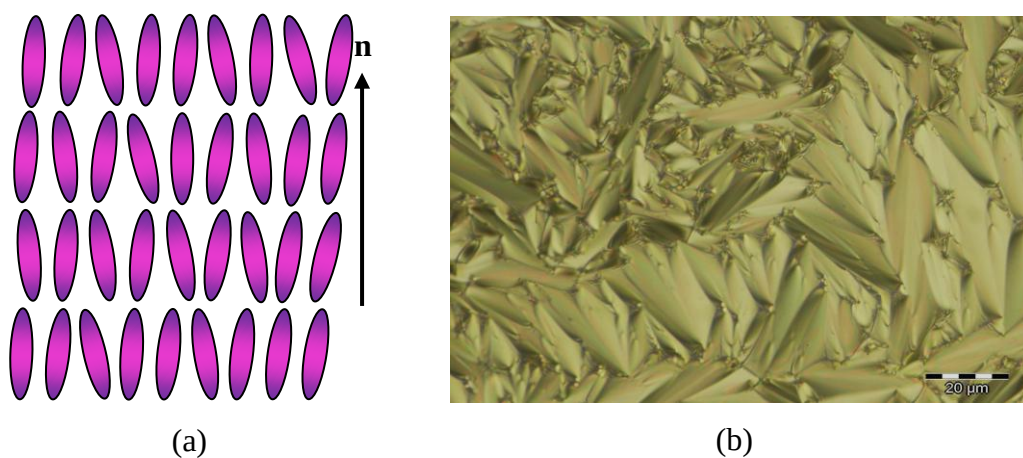


Figure 1.5 (a) Smectic A phase of liquid crystal. The long axes of the molecules in each layer, on an average, are perpendicular to the layer plane containing the molecules (b) optical micro texture of SmA phase.

SmC phase

On decreasing the temperature, the SmA phase transforms into a phase possessing lower symmetry. The breaking of symmetry may lead to tilting of the molecules relative to the smectic layers. The phase thus formed is the SmC phase. It is similar to the SmA phase except that director makes an angle other than 90° with the layer planes as depicted in fig.1.6.

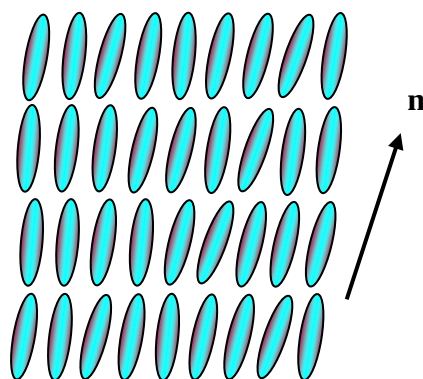


Figure 1.6 Smectic C phase of liquid crystal. The long axes of the molecules in each layer are tilted at an angle with respect to layer normal.

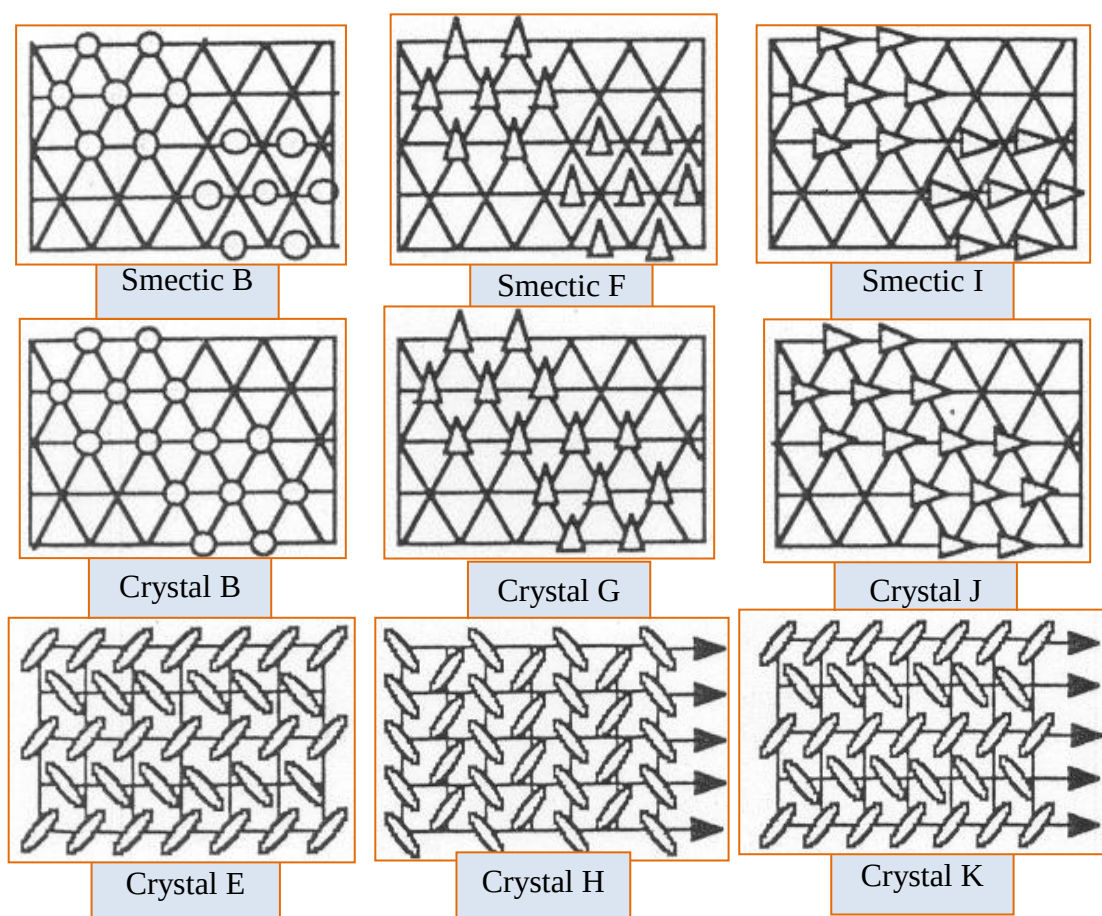


Figure 1.7 Structures of various smectic liquid crystal phases [14].

The tilt angle which the long molecular axis makes with the layer normal is a strong function of temperature. The detail of various other smectic phases is given in fig. 1.7.

1.3.3 Chiral phases

The molecules having no mirror image symmetry are known as ‘chiral molecules’. They are optical active in the sense that they rotate the plane of polarized light [7, 15-16]. Molecular chirality has strong influence on the LC properties. When chiral molecules are induced into LC phases, a variety of new phases is formed that have very unusual properties and hence chiral phases exist in place of non-chiral phase. Cholesteric replaces nematic phase and smectic phases are replaced by their chiral versions.

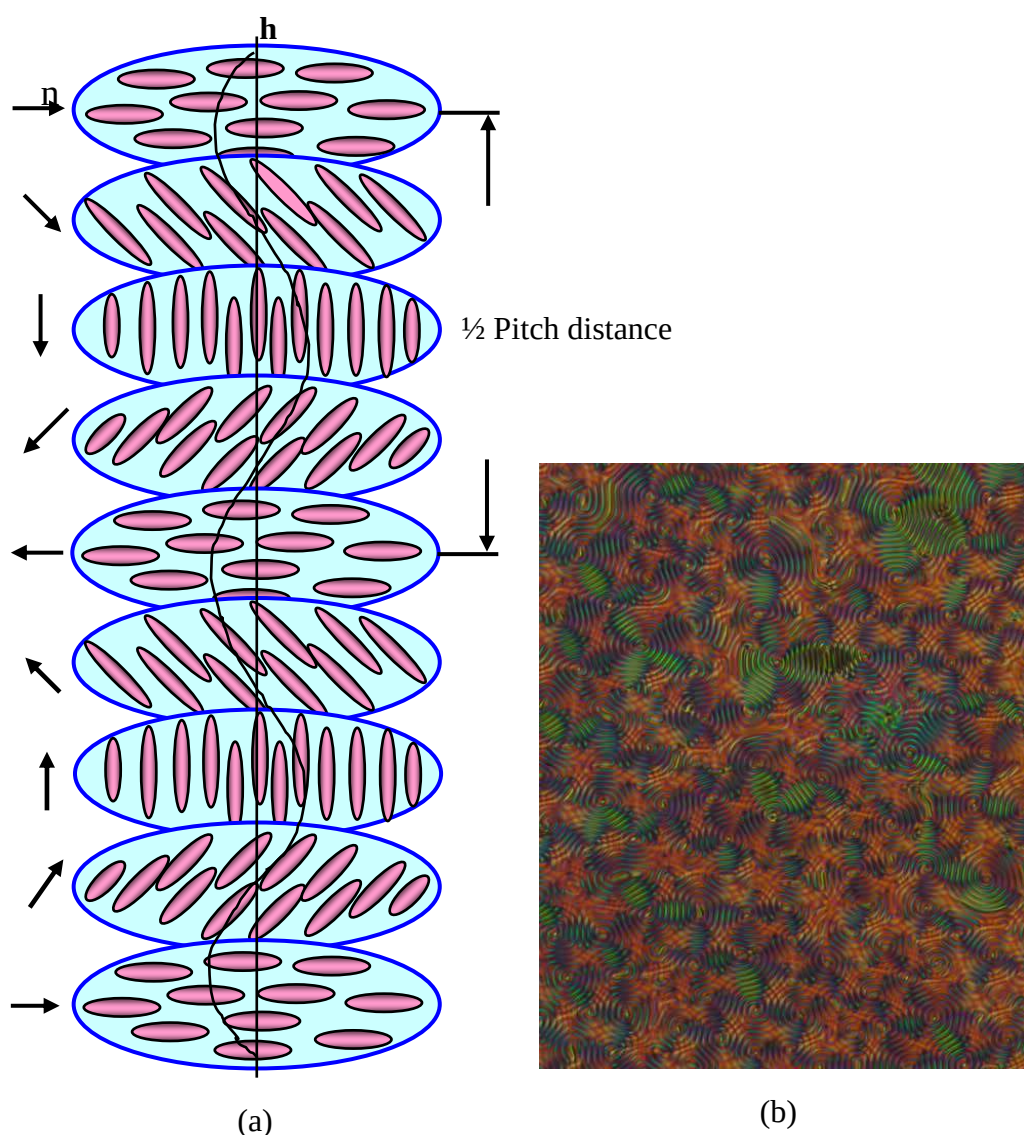


Figure 1.8 Schematic representation of molecular structure of (a) cholesteric liquid crystal (b) optical texture of cholesteric phase [17].

Chiral nematic or cholesteric phase

The chiral nematic or cholesteric liquid crystal phase is usually composed of nematic mesogenic molecules containing a chiral center; it produces intermolecular forces that favour alignment between molecules at a slight angle to one another. This leads to the formation of a structure which can be visualized as a stack of very thin 2-D nematic like layers with the director in each layer twisted with those above and below as shown in fig. 1.8 (a). In this structure, the directors actually form in a continuous helical pattern about the layer normal. An important characteristic of the cholesteric mesophase is the helical pitch, defined as the distance it takes for the director to rotate one full turn in the helix. The helical pitch controls the selective reflections of the cholesteric phase and makes them suitable for electro-optic display devices. The pitch can be adjusted to any desired value by adding appropriate amount of a chiral compound to a nematic structure. However, the necessary condition for the formation of a cholesteric mesophase is that the molecules are chiral (optically active). That is why cholesteric phase is also defined as the chiral nematic phase, represented by N*. The asterisk is used to differentiate a phase containing chiral molecules. When a chiral agent is mixed with a nematic liquid crystal, the pitch of the mixture is given by

$$p = 1/(\text{HTP} \cdot X_c) \quad (1.2)$$

This relationship, given by De Gennes and Prost [15], where HTP and X_c are the helical twisting and concentration of the chiral agent, respectively. HTP is mainly a characteristic parameter of the chiral dopant and depends slightly on the nematic host. The optical texture of cholesteric phase is shown in fig 1.8(b).

Chiral smectics phases

When optically active molecules are induced into smectic LCs, tilted smectic phase could generate a helical structure as a direct result of the molecular chirality of the constituent molecules. The chiral version of tilted smectic phases is known as chiral smectic phases. Chiral smectic phases can form different helical structures. In these phases, as position of tilt along normal to the layer is varied, the director rotates around the cone generated by the tilt angle. The rotation of the tilt is in the same direction for a given material and thus a macroscopic helix is formed [4-7].

In the chiral crystal smectic mesophases (SmG*, SmH*, SmJ* and SmK*), the helix is unwound by the crystal structure and chirality is suppressed [17]. So these phases cannot be used in devices. In case of low symmetry chiral smectic phases (SmC*, SmF* and

SmI*), the orientations of molecules tend to form a macroscopic helical structure while going from one layer to another [5]. Out of these, the chiral smectic C phase (SmC*) is most common smectic phase and is shown in fig.1.9.

Besides the above mentioned phases, we also have blue phases and frustrated or polar smectic phases.

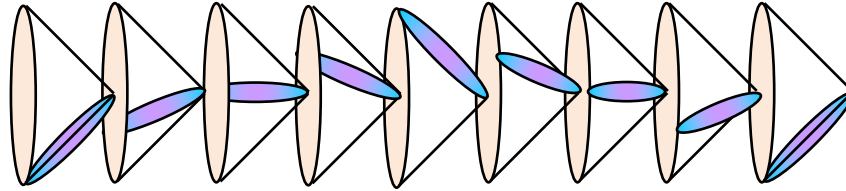


Figure 1.9 Modulated structure of chiral smectic C (SmC*) phase resulting in the helix formation [5].

1.4 PROPERTIES OF LIQUID CRYSTALS

1.4.1 Anisotropy

Due to presence of small degree of order among their molecules, LCs are anisotropic in nature. This property distinguishes the liquid crystals from ordinary liquids which are isotropic in nature. The anisotropy manifests itself in many physical (electrical, optical, magnetic) properties. Like, the LC behaves differently when subjected to an electric field depending upon whether the field is applied in a direction along or at right angle to the director. Also light (an electromagnetic wave) propagates differently through the LCs depending upon its direction relative to the director resulting into birefringence which is an important property of the liquid crystals [5-7]. The dielectric anisotropy is determined by the following relation

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} \quad (1.3)$$

where $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ represent the dielectric permittivity parallel and perpendicular to the LC axis respectively. The response of a LC to the applied electric field depends upon the sign and magnitude of $\Delta\epsilon$ [18-19]. If $\Delta\epsilon$ is positive, lowest energy state in the presence of field will be that in which LC axis is parallel to the field and for negative value of $\Delta\epsilon$, the lowest energy state will be the one in which LC axis is perpendicular to the field [5].

1.4.2 Birefringence

Liquid crystals show double refraction, i.e. they are birefringent. This is one of their important properties. The anisotropic nature of LCs is responsible for this phenomenon. When an electromagnetic wave passes through a medium, its wavelength and velocity decreases by a factor known as “*index of refraction*”. For anisotropic materials, the dielectric permittivity is different in different directions and hence two polarizations with different indices of refraction exist. Thus the light polarized along different directions travel through the material at different velocities as shown in fig.1.10. This optical phenomenon is called birefringence [20]. Fig.1.11 shows the different angles that polarization vector can make with the director field. The lines represent the director field and arrows show the polarization vector. If n_e and n_o are the refractive indices in the parallel and perpendicular direction respectively, then the optical anisotropy is defined as

$$\Delta n = n_e - n_o \quad (1.4)$$

If Δn is positive, the material is said to be positive uniaxial and if Δn is negative, it is said to be negative uniaxial. The biaxial materials have three indices of refraction [6].

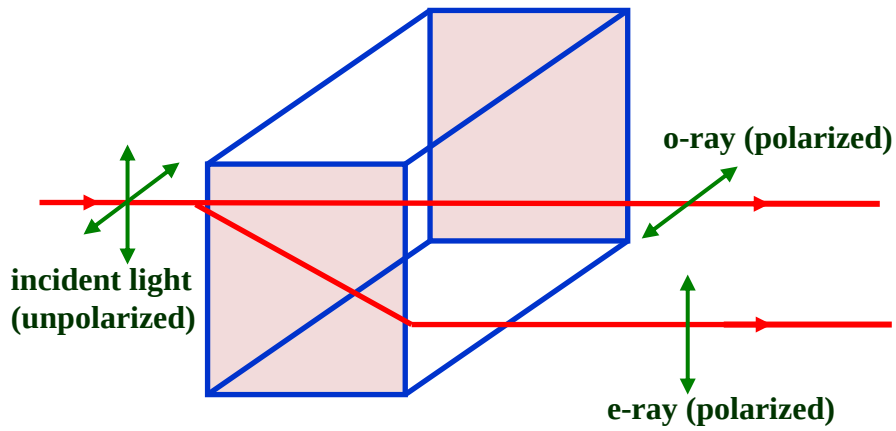


Figure 1.10 Incident light gets bifurcated into an ordinary and extra ordinary ray due to anisotropy in a birefringent material [20].

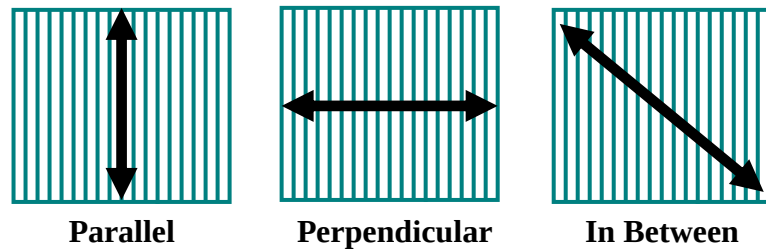


Figure 1.11 Different angles made by polarization vector with the director field [20].

1.5 FERROELECTRIC LIQUID CRYSTALS

Chiral smectic C liquid crystals possessing low symmetry are also known as ferroelectric liquid crystals (FLC). Ferroelectricity in them was first discovered by Meyer et al. in 1975 [21]. FLCs are the important systems from technical point of view due to their potential applications in electro-optic displays [22-23]. They are successfully used in fast response light shutters, image convertor, waveguides, alphanumeric displays and flat television screens. The molecules of FLCs possess permanent dipole moment. Meyer et al. demonstrate the origin of ferroelectricity both theoretically as well as experimentally in the SmC^* phase.

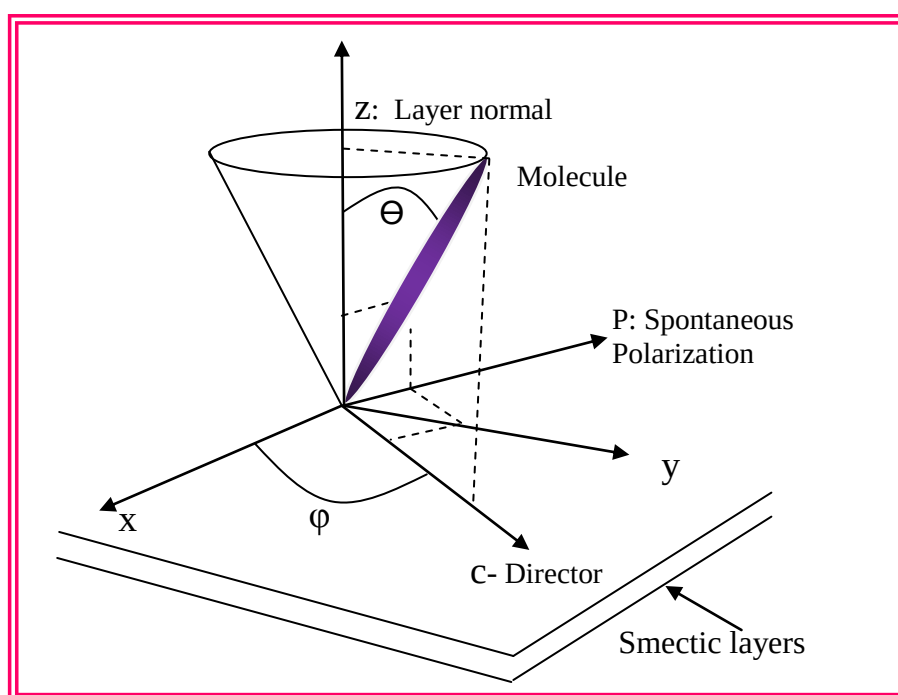


Figure 1.12 The geometry of ferroelectric liquid crystal molecule [7].

In the SmC phase, molecules are disordered within the layers as in SmA but inclined w.r.t. layer normal by an angle θ known as tilt angle as shown in figure 1.12 [7]. The structure has biaxial symmetry of monoclinic class with a plane of symmetry as indicated. Here θ is coupled with the layer thickness, whereas the azimuthal angle ϕ (angle between projection of director in the smectic plane and x -axis) is not. Thus, at any given temperature, the amplitudes of the tilt angle oscillations of the director are small as compared to those of azimuthal angle oscillations, with the result that the uniaxial symmetry about the mean molecular direction disappears and there exists only a plane of symmetry. Due to this, SmC is biaxial.

The chiral SmC (SmC*) phase is formed by the addition of optically active molecules in the ordinary SmC molecules. Although the SmC* phase is actually weakly biaxial, to a good approximation, it can be treated as a uniaxial material, just like the nematic phase which has an optical anisotropy Δn (birefringence). In this case the basic structure is same except that the molecular chirality causes a gradual rotation of the director of the molecular tilt. This rotation of director describes a helix. As a helix within the layer plane is incompatible with the layer structure, the helix axis must be parallel to the layer normal. There is no change in the amplitude of the tilt angle. The only variable that changes along the helix axis is the azimuthal angle or c-director i.e. the projection of the director into the layer plane. The periodicity of the helix is called pitch. It is temperature dependent but the variation behavior changes from compound to compound [24-26]. The director field in such a case is

$$n_x = \sin\theta \cos\phi \quad n_y = \sin\theta \sin\phi \quad n_z = \cos\theta$$

$$\phi = \frac{2\pi Z}{p_o} \quad (1.5)$$

where p_o is the pitch (2π rotation) of the helix and the layer normal is in Z-direction. This helical arrangement of the spontaneous electric dipoles has been also observed in helical ferromagnetic phases of some rare earths.

The helical structure present in the LC material is responsible for its interesting optical properties [27]. Firstly, the material gets an unusual strong optical activity. Secondly, a selective reflection can be seen in a planer aligned sample i.e. light with wavelength equals to that of the pitch and same handedness as that of the helix, cannot pass through the medium. If pitch length corresponds to that of the visible light, the sample will appear brightly coloured, as circular component of specific wavelength will be reflected. Another most interesting property of FLCs is that the symmetry of the SmC* phase permits the presence of spontaneous polarization within the layer plane and perpendicular to the director. Since spontaneous polarization is coupled with the director, it also rotates. It will lead to the cancellation of microscopic polarization in the bulk sample, but each layer is spontaneously polarizaed as shown in fig.1.13 [8, 28]. By supporting (unwinding) the helix with the electric field, this phase will exhibit macroscopic polarization and a true ferroelectric phase is generated and as a result net spontaneous polarization is obtained. Hence, these are also known as helielectric materials. The value of spontaneous

polarization in these materials is quite small, usually about one or two orders of magnitude less than that of a solid ferroelectric.

The coupling between polarization P and θ manifests itself above SmC^* to SmA phase transition: an electric field induces a tilt in the SmA phase as well. This is known as the **Electro-clinic effect**, and was first demonstrated by Garoff and Meyer [29]. Induced tilt angles as high as 10° have been observed in high polarization materials.

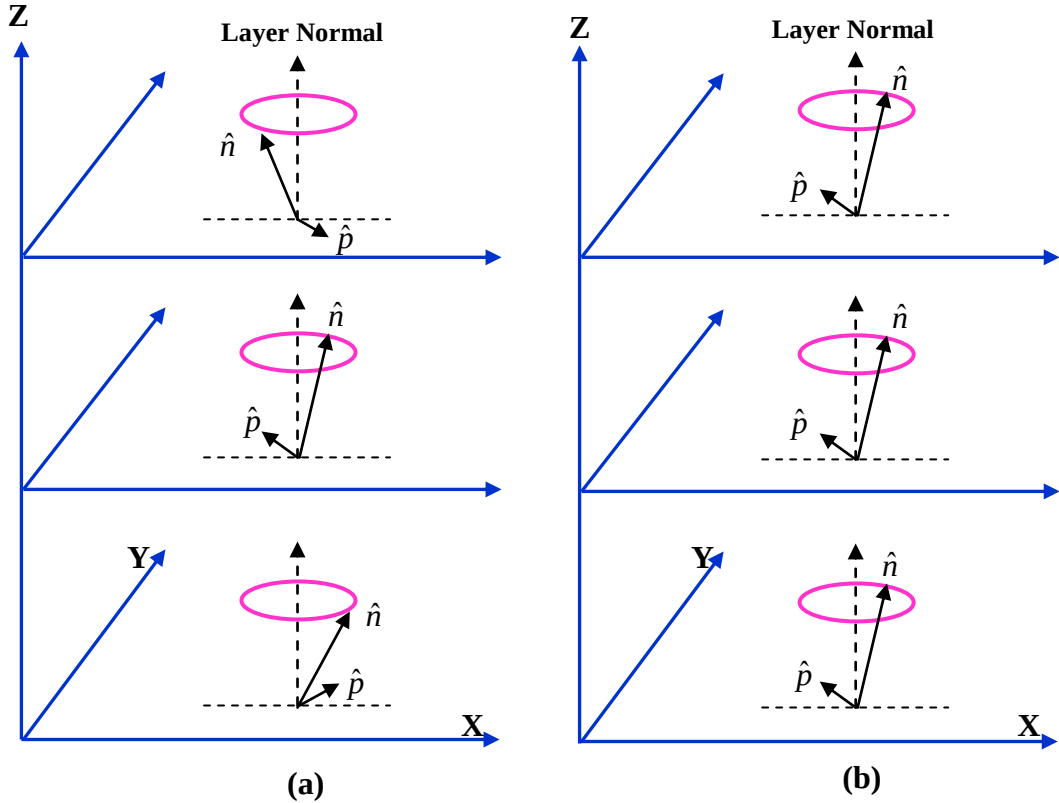


Figure 1.13 (a) Ferroelectric SmC^* structure and (b) Unwound SmC^* structure [8].

1.5.1 Origin of ferroelectricity in liquid crystals

The ferroelectric properties in solids were first discovered in Rochelle salt in 1921 and it was predicted that it possess various electrical, electro-optic and other physical properties [30]. This gave an idea to construct liquid ferroelectrics, but, however the search for ferroelectricity in liquids did not gain any ground as weak dipole-dipole interactions in liquids result in very small amount of polarization [17, 31]. To allow ferroelectricity to occur at a temperature T_C , the energy of dipole-dipole interactions p^2/a^3 (p is the dipole moment and ' a ' is the dipole separation) should be of the order of thermal energy $K_B T_C$. In dipolar liquids with relatively bulky molecules, p^2/a^3 is usually less than the thermal energy even at melting temperatures. Thus, the crystallization occurs before a

ferroelectric phase can be formed. In strongly polar liquids, dimmers are formed that results into an anti parallel arrangement of molecules and cancellation of the effective dipole moment. It prevents the occurrence of ferroelectricity and hence spontaneous polarization [17].

The head-tail invariance of liquid crystalline ordering due to weakness of dipolar interactions prevents the occurrence of ferroelectricity in high symmetry phases like nematic, cholesteric and SmA phases. In some biaxial liquid crystal phases, the symmetry is low enough to allow the existence of improper ferroelectric ordering, which is not the result of dipole interactions.

Meyer et al., in 1975, first discovered the ferroelectricity in low symmetry liquid crystalline phases. They construct liquid crystals with polar molecular ordering resulting from others and not from dipole-dipole interactions. In this case, the order parameter can be related to a certain type of molecular orientation and spontaneous polarization appears as a secondary effect [32].

The appearance of ferroelectric phase is assisted by the formation of structure (which is incommensurate due to modulation of polarization) in the spatial distribution of molecular axes, fig.1.13 (a). If the molecular orientation is subjected by the unit vector $\mathbf{n}$ (the director) then its direction would form a helix along the normal $\mathbf{Z}$ to the smectic planes. The spontaneous polarization, P_s , in the ferroelectric phase lies in the smectic layers in the direction of C_2 axis perpendicular to the director and layer normal $\mathbf{Z}$.

$$\mathbf{P} = P_o \vec{Z} \times \vec{n} \quad (1.6)$$

Hence the vector P_s is also rotated forming the helical axis along the normal to the layers. The reversal of sign in the tilt direction results in the reversal of sign of polarization.

1.5.2 Symmetry considerations in SmC and SmC* phases

Meyer explained in detail that the ferroelectricity of liquid crystal materials strongly depends upon the molecular structure. When the SmC phase is constituted of achiral molecules then the environmental or space symmetry consists of a centre of inversion described as C_{2h} . When the molecules of the phase are chiral, the local symmetry in layers is reduced to a polar C_2 axis i.e. the chiral LC molecules break the point symmetry of SmC phase from C_{2h} (2/m) to C_2 (2). This is one of the point symmetries allowing for ferroelectricity. As molecules are polar themselves, there is in-equivalence w. r. t. the dipoles along the C_2 axis. This occurs even though the molecules are undergoing rapid re-

orientational motion around their long axis. The time dependent alignment of the dipoles along the C_2 axis causes a spontaneous polarization to develop along this direction, parallel to the layer planes. Therefore each individual layer has a spontaneous polarization, which shows up in the direction of two-fold axis.

These arguments can only apply to individual layers, but when layers are stacked one on the top of the other, the tilt direction is rotated about the normal to the layer planes: consequently the layer polarizations are averaged out to zero and the phase cannot be described as helielectric. If the helix is unwound, the layer polarizations point in the same direction and hence phase becomes ferroelectric.

For this reduction in symmetry, the above arguments presented may be explained by figure 1.14 (fish) [6, 17]. It is assumed that in the layers of SmC^* , there are many molecules pointing up and down. This situation is represented by two asymmetric molecules that are shown as fish. If we assume that each molecule has a dipole pointing out of the eye of each of the fish, then dipoles are pointing in the same direction and the drawing has a twofold axis pointing out of the page. The shape of the molecules shows that the layer structure has no centre of inversion or mirror planes. Thus a degenerate structure with molecules pointing back into the page cannot be produced if the molecules are tilted in the opposite direction in the plane of the page with their dipoles pointing downwards.

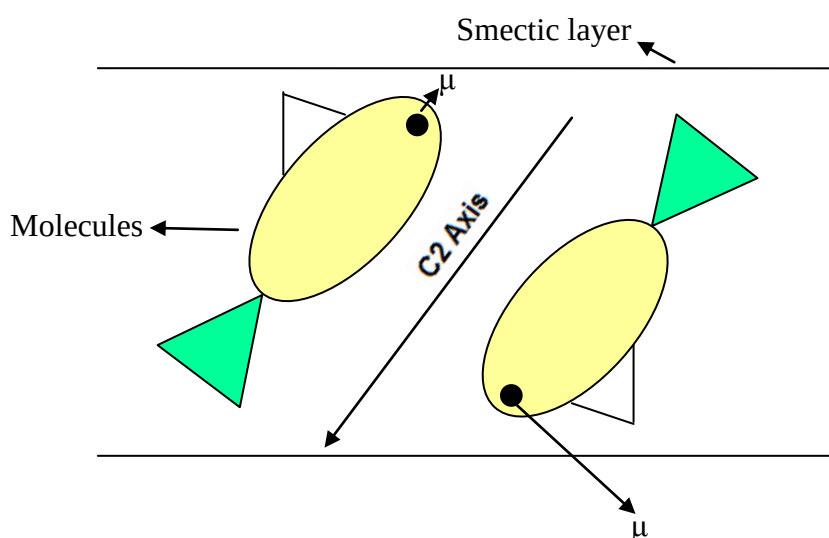


Figure 1.14 Reduced symmetry in SmC^* phase. The dipoles represented by μ are perpendicular to the plane of page and parallel to the C_2 axis [6, 17]. (Arrows represent the dipole moment and not the vector)

The polarization (P_X, P_Y, P_Z) is a polar vector. For polarization to exist in a given phase, the vector $\vec{P}$ must be invariant under all symmetry operations compatible with the phase in question. Let us explain that how this requirement clarify the fact that SmC^* is ferroelectric, whereas achiral SmC phase is not.

The X, Y, Z co-ordinates and the arrangement of molecules in SmC and SmC^* is shown in the following way [33].

<i>SmC</i>	<i>SmC*</i>
C_{2h}	C_2
$(P_X, P_Y, P_Z) \Rightarrow (-P_X, P_Y, -P_Z)$	$(P_X, P_Y, P_Z) \Rightarrow (-P_X, P_Y, -P_Z)$
$\Downarrow$	$\Downarrow$
$P = (0, P_Y, 0)$	$P = (0, P_Y, 0)$

In both the phases i.e. SmC (symmetry C_{2h}) and SmC^* (symmetry C_2), 180° rotation around the y-axis is an allowed symmetry operation.

Under this transformation, polarization vector transforms according to $(P_X, P_Y, P_Z) \Rightarrow (-P_X, P_Y, -P_Z)$. Since these two expressions must be identical, we can allow the possibility of a spontaneous polarization in the direction of the two fold axis: $P = (0, P_Y, 0)$. In the SmC^* phase the X-Z plane is a mirror plane.

Reflection in the X-Z plane [33]

<i>SmC</i>	<i>SmC*</i>
σ_{xz}	Reflection not allowed due to chirality
$(0, P_Y, 0) \Rightarrow (0, -P_Y, 0)$	$(0, P_Y, 0) \Rightarrow (0, P_Y, 0)$
$\Downarrow$	$\Downarrow$
$P = (0, 0, 0)$	$P = (0, P_Y, 0)$
Ferroelectricity not allowed	Ferroelectricity allowed

The existence of this mirror plane changes $(0, P_Y, 0)$ into $(0, -P_Y, 0)$ in the SmC phase. Since these two expressions must be identical, P must be zero and ferroelectricity is not allowed in the SmC phase. In SmC^* phase the molecules are chiral and are not any more mirror images of themselves. Thus, the XZ-plane is not any longer a mirror plane and ferroelectricity is permitted by the symmetry. The spontaneous polarization in the SmC^*

phase, points in the direction of the Y-axis. It lies in the smectic planes in a direction perpendicular to the tilt plane.

1.5.3 Symmetry considerations in other chiral phases

Number of compounds show different types of chiral phases (SmC^* , SmI^* and SmF^*) and crystal smectic mesophases (J^* , G^* , K^* and H^*), which could generate from geometry as a direct result of the molecular chirality of the constituent molecules. The chirality of all these chiral smectic mesophases takes the form of a helical structure but the helix manifests itself in a different way from the helix in the chiral nematic phase. In addition, to be substantially the most commonly exhibited of the tilted chiral smectic phases; the chiral SmC phase is by far the most important. There are also other chiral mesophases of smectic type (e.g. TGBA^* and $\text{SmC}^*_{\text{anti}}$ phases) [35].

1.6 FERROELECTRICITY IN OTHER TYPES OF LIQUID CRYSTALS

The ferroelectric phase is not only limited to SmC^* phase, it can be present in various types of LCs formed by the rod shaped (i.e. molecules one molecular axis is much longer than the other two) and disc shaped molecules (i.e. molecules with one molecular axis is much shorter than the other two). The ferroelectricity can also be present in achiral phase and it is purely due to the shape of the molecules as in case of banana shaped molecules. The rod shaped LC molecules possess ferroelectricity in single component as well as multi component compounds. The presence of ferroelectricity in various types of liquid crystals formed by the rod shaped molecules and other type of molecules is discussed here.

1.6.1 Rod shaped molecules

Single component ferroelectric liquid crystal systems

According to the simple symmetry consideration of Robert Meyer and strict theoretical group analysis, the presence of spontaneous polarization is possible in any system having lamellar structure and consisting of tilted chiral and dipolar rod like elements. A non-zero average dipole moment perpendicular to the plane of the molecular tilt results due to appearance of symmetry and hindered rotation around their long molecular axes.

Majority of synthesized ferroelectric liquid crystals consist of molecules which meet simultaneously all requirements necessary and sufficient for the appearance of

spontaneous polarization (P_s). The conventional way to synthesize a liquid crystalline ferroelectric is to look at achiral tilted smectic phase e.g. SmC and tries to synthesize a chiral analogue. In many cases chirality is due to asymmetric C-atom. The temperature range of SmC* phase does not markedly differ from that of SmC phase [31].

Cahn, Ingold and Prelog [36] produced an invaluable and universally used method of defining and labeling chiral centers in the molecular structure. An archetypical structure of a chiral, calamitic, rod-like liquid crystalline compound, which has two flexible aliphatic chains attached to a rigid aromatic or quasi-rigid alicyclic core is shown in fig.1.15. The chirality of this compound with respect to the rules of Cahn et al. is determined by the atomic numbers of the substituents Y and Z. However, the other aspects of molecular chirality are also important in LCs in determination of phase structure type and phase characteristics. The first SmC* material used to establish ferroelectric properties in LCs was DOBAMBC (p-decyloxybenzylidene-p'-amino-2-methylbutylcinnamate) in 1974 [5].

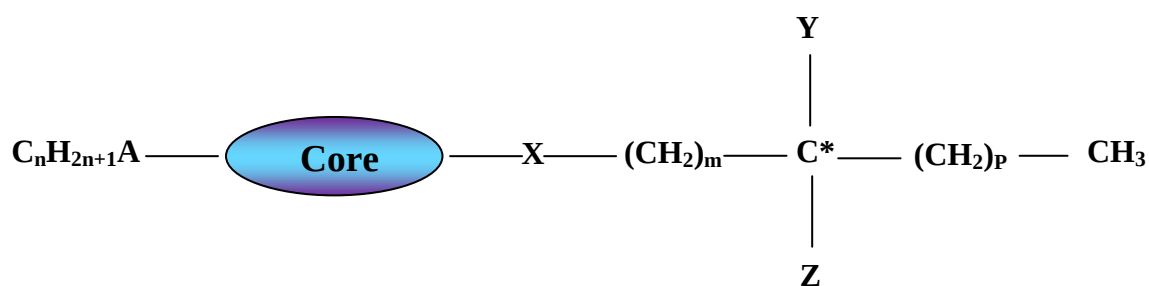


Figure 1.15 A typical structure of a chiral, calamitic, rod-like liquid crystalline compound. Here n, m and P are integers; (B+m) is the parity; A and X are polar groups; Y and Z are different substituent; * denotes a chiral centre [36].

A majority of synthesized FLCs consists of molecules, which met all the requirements necessary and sufficient for the appearance of P_s . The use of ester and ether moieties provide the necessary lateral dipoles for molecular tilting and use of the conjugated cinnamate and Schiff's based linkage groups enhanced the polarizability to ensure the generation of LC phases. DOBAMBC received much attention but it was found to be photo chemically unstable, had a relatively high viscosity and a very low P_s and thus unsuitable for use in devices. Later on, analogous to DOBAMBC, Schiff base compounds were prepared which enhanced the understanding of molecular structure on phase morphology, transition temperature and magnitude of P_s [5-6].

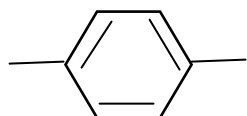
Multi component ferroelectric liquid crystal systems

The conditions which are sufficient for the origin of P_s may be satisfied not only in single compounds but in binary or multi-component mixtures as well. The structures of chiral materials, mesogenic or not, that are suitable for use in ferroelectric mixtures are summarized by the template as shown in fig.1.16 [5].

Common terminal chain units

$C_6H_{13}O$, $C_8H_{17}O$, C_9H_{19} , $C_5H_{11}OCH_2$

Common units found within the core



Common chiral centre unit combinations

R = C_2H_5 , C_6H_{13} , $C_6H_{13}O$

X = $-O-$, $-CH_2-$

Y and Z = H, CH_3 , CN, F, CF_3 , Cl

The most important case corresponds to mixtures of non-chiral SmC compounds with chiral dipolar additives. Such mixtures have the same point symmetry (C_2) which is typical of single component FLCs. Thus, the mixtures composed from non-ferroelectric components are ferroelectric and the value of P_s can be of the same order of magnitude or even higher than that for single component liquid crystals [31]. However the mechanism for dipolar ordering is similar in two cases.

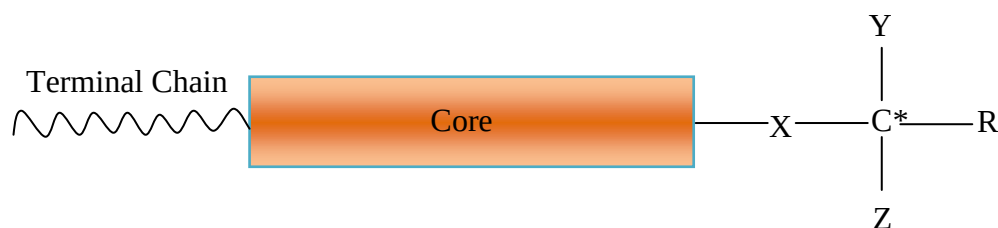


Figure 1.16: General structure of chiral materials for ferroelectric mixtures [5].

The main interests revolve around the need of chirality, a low viscosity, a high P_s and the generation of SmC* phase over a reasonable temperature range. Such conflicts of interest have been recorded in a wide range of other types of chiral materials for ferroelectric applications. These chiral materials are often difficult and expensive to synthesize.

Accordingly, the use of a single chiral material does not suffice for a commercial device and in fact, neither does a mixture composed entirely of chiral materials. However, from a practical point of view it is much easier to synthesize separately achiral SmC matrices and chiral dipolar additives. These matrices should satisfy only some requirement with respect to the temperature range e.g. stability, optical properties etc. The chiral dipolar additives determine the P_s value and must have complicated molecular structure which may be non-mesogenic.

The material requirements to be used as a good ferroelectric host mixture or matrix are; low melting point (below room temperature), wide SmC range with no underlying ordered smectic phases, cooling phase sequence of I – N – SmA – SmC, low viscosity, tilt angle of 22.5° , low to moderate optical anisotropy, negative dielectric anisotropy, high dielectric biaxiality and high chemical and photochemical stability.

Of all the materials that exhibit SmC phase, only minor is ultimately suitable for use as ferroelectric host materials. Currently, the best host materials for use in ferroelectric host mixtures are the phenylpyrimidines and materials based on the ortho-difluorophenyl moiety (e.g. difluoroterphenyls and difluorophenylpyrimidines) [31].

After the selection of matrix for ferroelectric mixtures, a chiral dopant is required. The chiral dopant should provide some additional physical properties to the ferroelectric mixture as listed above i.e. reasonably high spontaneous polarization (P_s), long pitch and good solubility and compatibility between host and dopant.

The chiral dopant need not to be mesogenic but should have a mesogenic like structure, preferably similar to the structure of host materials (to maintain the properties of the host mixture). Consequently, some of the most interesting chiral materials in LC mixtures are not liquid crystalline or at least their LC phases are less important than their effects on the physical properties of the ferroelectric mixture.

Materials including ester moieties and terminal alkoxy chains are well known for generating the tilted SmC phase because of lateral dipoles. Not surprisingly, chiral analogues of such esters produce the chiral SmC phase.

Another technique to form ferroelectric mixtures composes from an achiral tilted SmC matrix with dipolar molecules and chiral but non-polar additives. One other way is to combine a chiral non-polar SmC* with achiral but strongly polar impurities. However these two methods do not result in high value of spontaneous polarization because of weak coupling between chiral and dipolar moieties.

Most research emphasis is applied to chiral materials (not necessarily mesogenic) for use as dopant in ferroelectric mixtures. However, for more fundamental studies on single materials, the generation of SmC* phase is essential. The most important chiral dopants for ferroelectric mixtures have a polar group on the chiral centre (e.g. Cl, F, and CN). The chloro-substituted material has the additional advantage for high P_s in having an adjacent polar carbonyl group but is extremely unstable, which is a major disadvantage [37-41]. However, the fluoro-substituent has widely employed at a chiral centre in dopant materials because of its small size and high electro-negativity. Ferroelectric host materials are often based upon phenylpyrimidines. Accordingly, an enormous range of chiral phenylpyrimidine systems have been prepared and most of these have a fluoro-substituent at the chiral centre in order to provide a reasonably high P_s (10 nC/cm² with 20% dopant) and yet retain the SmC* phase stability of the host mixture (which is rather low). Other, more unusual chiral materials have been prepared as additives to ferroelectric mixtures.

In the above discussion, one can view that a room temperature multi component ferroelectric material can be composed from high temperature compound of various classes.

Polymeric ferroelectric liquid crystal systems

Polymer liquid crystals (PLCs) composed of two independent sub-systems: mesogenic fragments and side chains [42-45]. The flexible chain does not influence the static parameters e.g. refractive index and magnetic susceptibility etc. When mesogenic moieties form a structure that is necessary and sufficient for the ferroelectricity, spontaneous polarization appears in liquid crystals. PLCs are usually made chiral by incorporating a chiral moiety within the structure. Chiral PLCs are commonly designed and synthesized to exhibit the SmC* phase because of their potential use as non-linear electro-optical materials or as pyro-electric detectors. The comb-like polymers were synthesized with aim of producing ferroelectric structure. Fig1.17 shows comb like polymer with lateral mesogenic unit [17, 46].

Such ferroelectric polymers have a P_s and can be switched. However, PLCs have some specific features like (i) P_s and pyro-effect that remains even in the glassy state (ii) mono-domain state in SmC* which relax very slowly due to the high viscosity of polymers etc. Near the transition temperature to SmA phase, the soft mode relaxation time is strongly extended. The main features of ferroelectricity in low and high molecular weight

compounds are similar. However, the presence of spontaneous polarization in the glassy state opens up the possibilities for investigation and technical application of pyroelectric and piezoelectric properties of corresponding solid films. In addition the polarization measurement allows the mutual influence of flexible chains and mesogenic moieties to be studied. The higher viscosity of these systems increases the switching times by two orders of magnitude longer than their low molecular analogue [45]. To reduce the viscosity and improve the switching time, low molar mass (LMM) liquid crystals are being preferred and used. They have properties in between the properties for FLCs and PLCs. These are known as oligomeric liquid crystals.

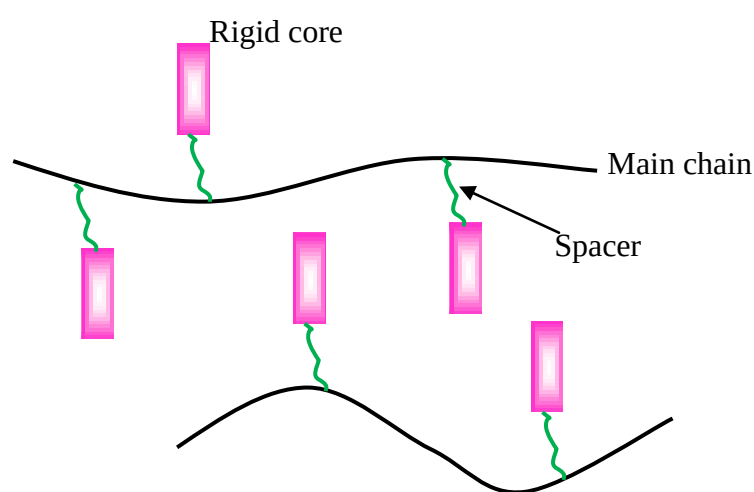


Figure 1.17 Structural model of comb like polymer with lateral mesogenic unit [17].

1.6.2 Disc shaped molecules

In disc-shaped molecules, one molecular axis is much shorter than the other two. Earlier, after the discovery of liquid crystals, it was thought that only the molecules having rod-like structure could generate mesomorphism. However, later in 1970, the existence of mesophases generated by disc-like molecules was predicted theoretically. Chandershekhar et al. in 1977 reported the mesomorphism in disc-shaped molecules (hexa-alkanoylbenzenes) [47]. Such compounds are called discotic LCs and again rigidity in the central part of molecule is essential [48-49]. The core of typical discotic liquid crystal molecule is usually based on benzene, triphenylene or truxene with 6 or 8 chains, each resembling a typical calamitic LC molecule. Fig.1.18 shows the general structural template for discotic LCs.

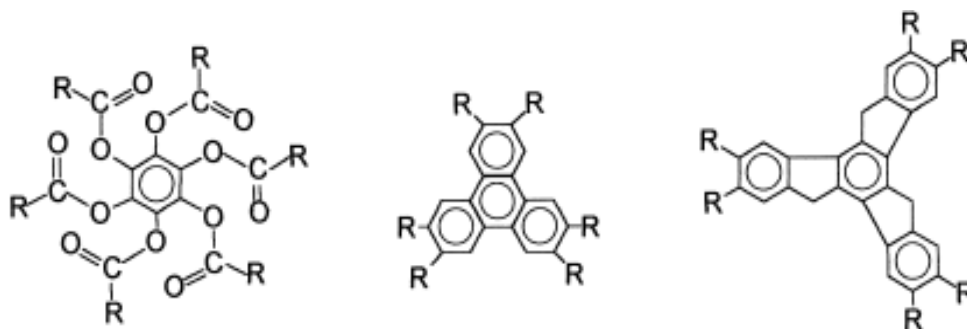


Figure 1.18 A general structural template for discotic liquid crystals [50].

The disc shaped central core unit is usually benzene or a polyaromatic such as triphenylcyanine, but columnar phases have been generated with alicyclic cores such as cyclohexane and carbohydrate. In order to maintain the disc-like structure, the central core is usually symmetrical and the peripheral dendritic units are present in numbers that are appropriate for the central core.

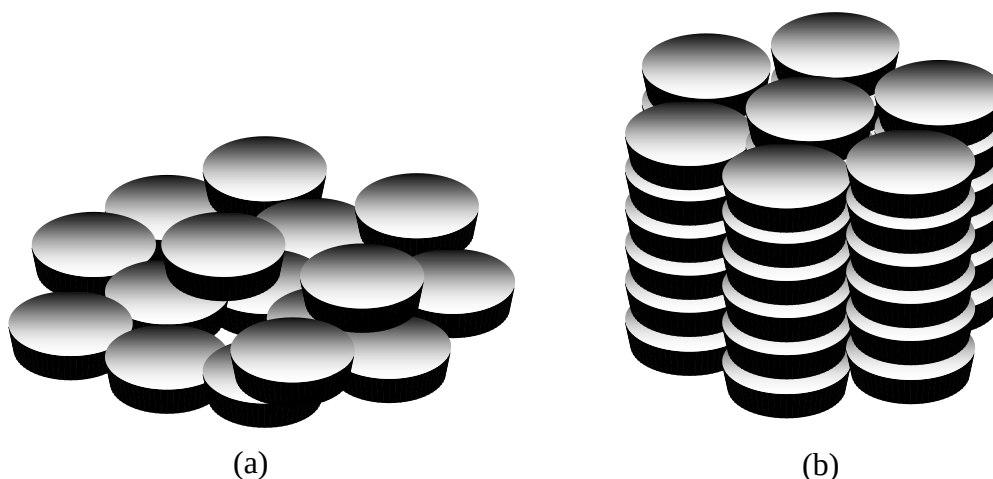


Figure 1.19 Disc shaped molecules in (a) nematic and (b) columnar discotic liquid crystals [48-49].

Discotic liquid crystals are basically of two types: nematics and columnar liquid crystal phases. Relatively few examples of chiral discotic nematic compounds exist, probably because of the perceived lack of applications for discotic systems and the relative expense of chiral units. The chiral nematic discotic phase has an analogous structure to the calamitic chiral nematic phase with gradual rotation of the molecular director through the phase that describes a helix. The polymorphism found in columnar phases is similar to that found in smectic mesophases generated by nematic liquid crystals. Columnar liquid crystals are generally one-dimensional fluids where disc or pyramidal shaped molecules

form fluids. There is short range translational order along the molecular axis and long range hexagonal or rectangular order in the direction normal to it. The disordered molecular columns may be aligned homeotropically in a narrow cell on cooling from the isotropic phase, with the stacks perpendicular to the substrates that form the walls of the cell. The discotic systems can be made chiral by incorporating a chiral unit into one or more of peripheral units that surround the discotic core [51]. Depending upon the structure of molecular orientation with respect to molecular axis and on lattice structure, a number of columnar phases are distinguished. Among them, quite a few are ferroelectric. “J. Prost” predicted the occurrence of ferroelectricity in columnar phases theoretically. As a prerequisite for this phenomenon, the disc like molecules will have to be chiral and tilted to the columnar axis. The first experimental verification in this regard was given by Bock in 1992 [52-53]. Scherowsky, Chen and Heppke et al. then observed the similar electro-optic effects on other compounds. These tilted columnar phases have same C_2 symmetry axis as in case of SmC^* LCs or 3D crystal Rochelle salt and P_s is parallel to the C_2 axis i.e. perpendicular to the column axis and the tilt plane. P_s is generated because of the restriction in rotation of the peripheral chiral chains. It was suggested that these columnar phases can be switched by electric field and are ferroelectric [52].

1.6.3 Banana shaped molecules

Niori et al. [54] observed the first obvious example of ferroelectricity in a smectic phase formed by achiral bent core (banana-shaped) molecules which have accepted as single new ferroelectric liquid crystals. The ferroelectricity is attributed to the polar packing of molecules with C_{2v} symmetry where the molecules are packed in the same direction. Weissflog et al. have reported that ferroelectricity could be detected only for one of the phases in some liquid crystals consisting of achiral banana shaped molecules. The existence of such a mesophase depends upon the length of the rigid core of the molecules as well as on the magnitude of the bend and its position. Recently it has been reported that the smectic phase of achiral banana-shaped molecular systems could form helical substructures [55]. On one hand, Link et al. [56] reported that achiral molecules with bent cores could form a chiral layer structure with a handedness that depends on the sign of the tilt and on the other hand, Sekine et al. [57-58] reported an achiral banana-shaped molecular system in which helical domains of both handednesses are formed in the smectic phases.

Matsunaga and co-workers [59] synthesized some banana-shaped materials and found that they can form smectic LCs but they did not pay any attention to the electrical properties. Watanabe et al. [60-61] reported that a ferroelectric smectic phase with C_{2v} symmetry might be formed for some main chain types of LC polymers, if two different aliphatic spacers with odd numbers of carbon are incorporated into the backbone in a regularly alternating fashion and they segregate into different mono-domains. Niori et al. reported the ferroelectricity in the SmA_b phase of a material consisting of banana shaped achiral low weight molecules (SmA_b phase is similar to SmA phase and is biaxial). They prepared homologous series of banana shaped molecules and then discovered the ferroelectricity in the SmA_b and $HexB_b$ phases. These materials, which form smectic phase are particularly interesting because of their shape, they form a peculiar smectic phase in which the banana-shaped molecules are closely packed and are aligned in the direction of bending. A typical banana shaped structure is shown in fig.1.20.

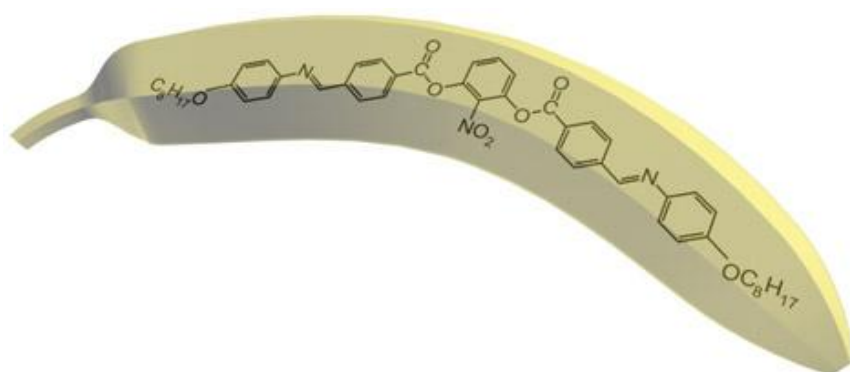


Figure 1.20 Geometry of banana shaped liquid crystal [62].

1.6.4 Ferroelectric liquid crystal oligomers

Liquid crystal oligomers consist of molecules containing two or more mesogenic units connected via flexible spacers, most commonly alkyl chains. These oligomeric liquid crystals are important from the view point that these possess the properties of both monomer as well as polymer, like fast switching and glass transition temperatures [63-66].

In the literature, examples of chiral liquid crystal compounds are dominated to large extent by the low molar mass monomeric materials and a lesser extent by the chiral polymer liquid crystals. However, only side chain liquid crystal polymers are found to

show the ferroelectricity. The examples of chiral liquid crystals oligomers are scarce. The studies already carried out are mainly confined to the influence of chiral flexible spacer on the phase behaviour of liquid crystal oligomers or have examined the induction of chiral nematic phases in nematic host by the addition of non-mesogenic oligomers with chiral spacer [67-70].

1.7 FERROELECTRIC LIQUID CRYSTAL STRUCTURES

1.7.1 Surface stabilized ferroelectric liquid crystals (SSFLCs)

SSFLC structure was reported by Clark and Lagerwall in 1980 which shows very fast bistable electro-optic response with threshold [71]. In this structure the pitch (p) of the FLC material is greater than the cell thickness (d) i.e. $p > d$. The basic SSFLC structure combines three appropriately chosen features (sample thickness, layer direction and boundary conditions) as shown in fig1.21 [71-76].

In FLCs, the layers are oriented perpendicular to the conducting glass plates so that the electric field vector is in plane of rotation of polarization P . In this geometry, the helix can be ‘elastically unwound’ if the sample surfaces are treated to enforce any particular director orientation. A sample can also be made thin enough, smaller than the helical pitch of the order of few microns, if the boundary conditions are chosen that the molecules have preference to align parallel to the bounding glass plates. The result of the combined constraint on the molecules at the surface to lie on the tilt cone and simultaneously in the surface, results in two preferred distinct but structurally equivalent director reorientations. These two stabilized states can be denoted by up (+ P) and down (- P) as indicated in fig.1.21 [75]. Switching of one state to another state is achieved by reversing the direction of the applied electric field. Since these are stabilized states, adjacent regions of opposite orientation will be separated from each other by distinct boundaries as illustrated in fig. 1.21, which in analogy with similar structures in crystalline ferroelectrics and ferromagnets are called the domain walls. However a clear distinction can be drawn between SSFLC domain walls and those found in crystals, SSFLC domain walls are stabilized by surface interactions and not by bulk anisotropy. Indeed, De Gennes and Pincus have shown that domain walls are not possible in the bulk in a variable with continuous orientational degeneracy. Pursuing the magnetic analogy further, the domain walls are “Bloch like” if directed along the smectic layers and “Neel

like” if normal to the layers. Fig.1.21 shows the ideal bookshelf geometry o SSFLC layers sandwiched between the LCD substrates, as suggested by Clark and Lagerwall.

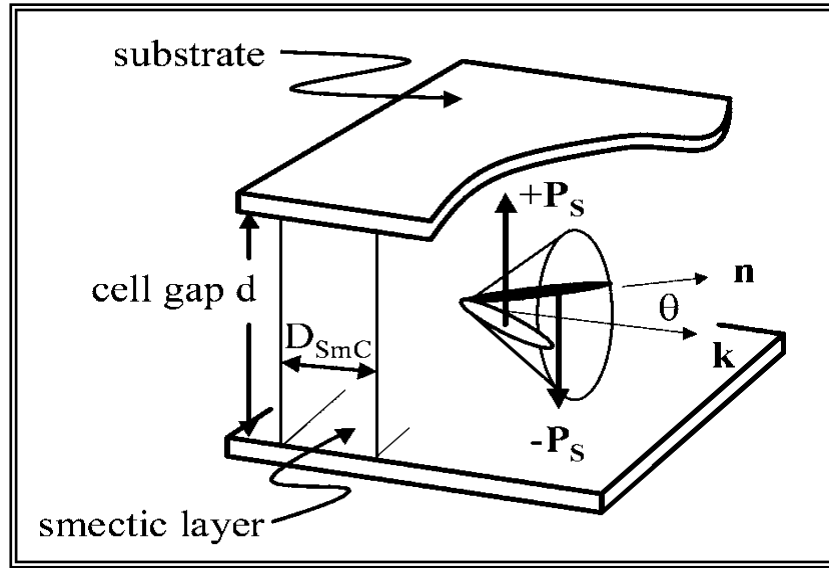


Figure 1.21 Schematic surface stabilized ferroelectric SmC* liquid crystal geometry with tilt angle θ (T) and spontaneous polarization P_s (T) [75].

Thus with the helix unwound, a ferroelectric smectic in the SSFLC geometry behaves optically essentially as a uniaxial slab with the uniaxis along the director orientation $\mathbf{n}$. The simplest geometry has the sample between crossed polarizers with $\mathbf{n}$ parallel to the polarization direction in the down state leading to extinction of light passing through the polarizers and sample (down=off).). In the up state, the polarization will make an angle 2θ with the optic axis and the fraction of the optical power I will be

$$I = I_0 [\sin(4\theta) \sin(\pi \delta n d / \lambda)]^2 \quad (1.7)$$

Where δn is the refractive index anisotropy, λ is the vacuum optical wavelength and I_0 the parallel polarizer transmittance. Clark et al. [77] used the compounds DOBAMBC and HOBACPC for these studies in SSFLC configuration. The absence of helix in the SmC* phase was explained and the electro-optic response was characterized by the motion of domain walls separating regions having apparent optic axis. The motion of domain walls was observed by slowly varying the applied voltage. The bistability was also studied by applying pairs of opposite polarity rectangular voltage pulses of selectable amplitude, width and time separation to the sample.

It was explained that the effect of switching is to rotate the uniaxis about the normal to the surface through an angle of twice the tilt angle. In order to obtain bistability, boundary conditions that constraint the molecules to be parallel to the plates, but allow several or continuous orientations about the normal to the plates are required. The SSFLC is the first LC electro-optic structure to employ such a combination of strong-weak boundary conditions.

The stable alignment states of the FLC can be determined by the boundary condition at the FLC-polymer film interface. In addition, the interaction at the boundary also involves the smectic layer structure. These functions of the boundary produce some problems such as zig-zag defects or the dependence of the switching behavior. Bawa et al. [72] has explained the elimination of zig-zag type defects of SSFLC cells by applying alternating electric field of suitable frequency to the polymer rubbed glass substrates.

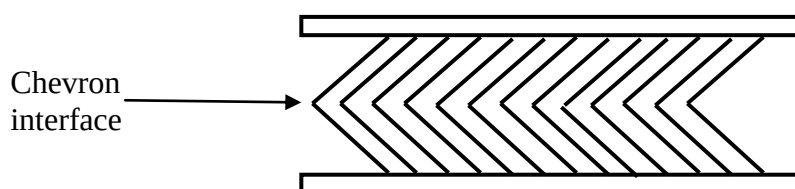


Figure 1.22 Chevron layered stacking in SSFLCs [71, 77].

Clark and Lagerwall explained that ‘bookshelf’ texture can be readily obtained in SmA phases but, on cooling to SmC, the texture changes because layer distance decreases [71, 77]. The most common resulting texture is a vertical chevron texture with a kink of the layers at the mid plane of the film. Figure 1.22 shows the chevron geometry obtained in SSFLC. The contrast and homogeneity of displays with horizontal chevron texture is significantly better than in samples with the normal chevron texture. In spite of high optical contrast and fast switching speed, the SSFLC structure has too many drawbacks and attempts were made to obtain better structure for the electro-optical effects.

1.7.2 Soft mode ferroelectric liquid crystal effect (SMFLC)

The basic difference between soft-mode and SSFLC structure is that for SSFLCs, θ remains constant and ϕ varies (called Goldstone mode) while for SMFLC, ϕ remains constant and θ (called soft mode) varies. The SSFLC exhibit bistability while SMFLCs show continuously controllable intensity change as the SMFLCs employs the SmA*

phase while SSFLC employs the SmC* phase. Thus uniform alignment in SMFLC is easier to obtain than SSFLC even if the cell is as thick as 10 μ m [78].

1.7.3 Deformed helix ferroelectric liquid crystals (DHFLCs)

In 1989, Beresnev et al. proposed another linear electro-optic effect in ferroelectric chiral SmC LCs i.e. deformed helix ferroelectric (DHF) effect [79]. The DHF effect is complimentary to SSF effect. The DHF cell employs a LC material whose pitch length is about tenfold shorter than the cell gap. Moreover, the surface anchoring is kept weak so that the SmC* helix is retained within the cell boundaries and the bookshelf structure is generated where the smectic planes are oriented perpendicular to the glass plates. It is a linear effect i.e. it has no inherent stability. They operate at much lower voltages and with shorter response times than SSF-LCDs. Funfschilling et al. explained that the distortion of the helix by the applied electric field is responsible for this electro-optical effect; if the pitch is shorter than the wavelength, distortion leads to a change of the effective refractive index [80]. Unwinding of helix is one of the limitations of this effect. The director configuration of the DHFLC cell is shown in fig.1.23 [80-84]. The planer cell contains a chiral SmC LC with its helical axis oriented parallel to the substrates. In the absence of the electric field, one axis of the effective refractive index (averaged over many turns of the pitch) coincides with the helical axis. This critical voltage is determined by

$$V_{th} = \frac{\pi^4}{4} \frac{K}{dp_c} \left(\frac{d_l}{p_o} \right)^2 \quad (1.8)$$

where K is the effective elastic constant, θ_o is the SmC* tilt angle, d_l is the layer thickness, $q = 2\pi/p_o$ is the wave vector corresponding to the unperturbed pitch p_o and p_c is the piezoelectric polarization of the SmC* LC.

It was explained that DHFLCs are less sensitive to surface treatment than to Clark-Lagerwall effect. The insensitivity of the DHF-LCD to the surface treatment enables to utilize successfully the common aligning techniques for producing homogeneous alignment on the substrates like rubbing, oblique evaporation etc. High quality orientation is easily obtained which provides a contrast ratio up to 100:1 or even more.

The basis of DHF is as follows: If surface interactions are weak, the equilibrium structure of a SmC* LC is helix i.e. the director as well as the P_s spiral around an axis perpendicular to the smectic planes and parallel to the plates of the device. If the helix

pitch is shorter than the wavelength of light, the refractive index is an average over the helical structure. Since the helix is easily distorted by the electric field, it is possible to electrically affect the average effective birefringence.

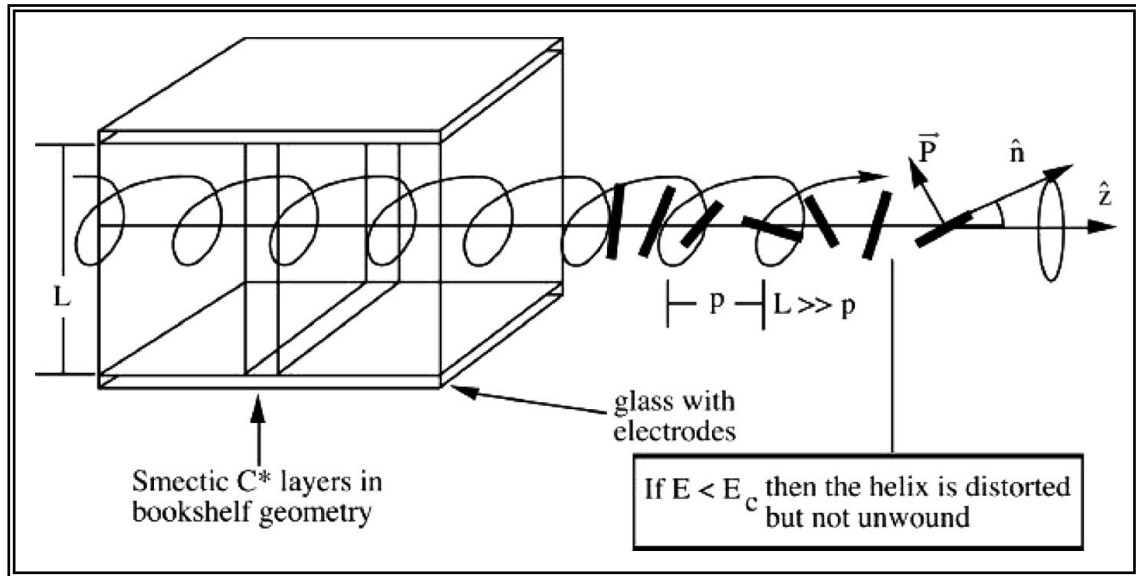


Figure 1.23 Schematic geometry of deformed helix ferroelectric SmC* liquid crystal [81].

Funfschilling et al. [84] discussed the electro-optics of the DHF effect, emphasizing the large electrically induced changes of birefringence which occur in DHF-LCDs with large switching angles. Based on these results a new DHF operating mode was introduced which allowed DHF cell gaps larger than the $5\mu\text{m}$ cells. A second new type of DHF-LCD was presented which was used for low tilt angle DHF materials. This second, double layer DHF-LCD allowed fast, bright, ghost free, low voltage operation. They also reported the influence of various material parameters and their temperature dependence on DHF display. It was shown that pitch below 150 nm at room temperature is required for high contrast DHF-LCDs.

1.7.4 Short pitch bi-stable ferroelectric liquid crystals (SPBFLCs)

Almost all reported LCDs, so far, based on FLCs are SSF type. The main key requirement of the LC material for this device is a pitch length more than the sample thickness. The materials with high polarization usually have short pitch. The DHF effect is linear and has no inherent bi-stability. Funfschilling et al. achieved to obtain bi-stability

in these short pitch materials. This new effect was termed as short pitch bi-stable effect. The likely molecular configuration of SBF-LCD and one of the two stable director configurations in the plane of SBF-LCD substrate are shown in the fig.1.24 (a, b) respectively [84]. The switching angle of SBF-LCD is nearly 45° , which results into optimum on-state brightness. For this large memory tilt angle, it was concluded that the chevron formation if at all present does not affect the brightness and contrast to the extent as in case of SSF-LCDs.

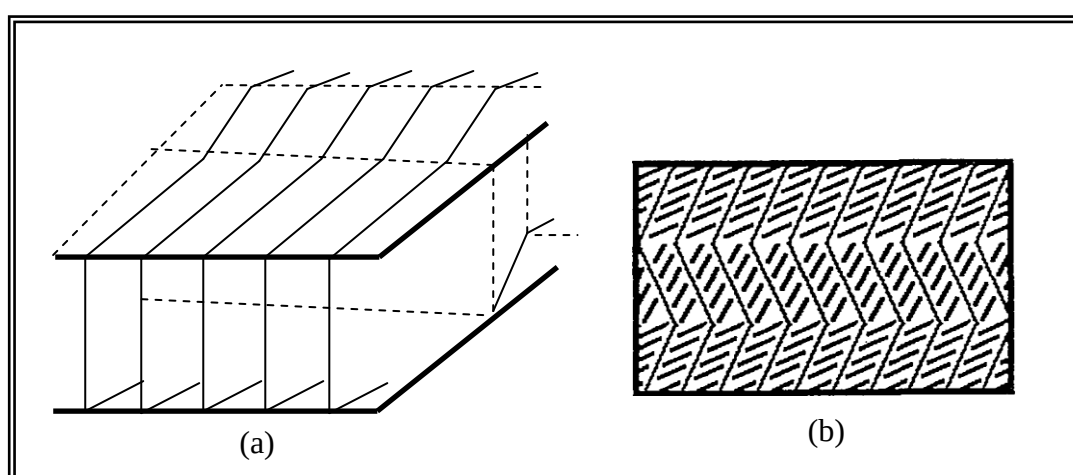


Figure 1.24 The short pitch bi-stable configuration [84].

Because of the large P_s of SBF liquid crystal materials, low electric fields are sufficient to induce helix unwinding in SBF-LCDs. Except for bi-stability, the molecular configuration of SBF-LCDs is related to the high field configuration of DHF-LCDs. The peculiar molecular conformation of the SBF suppresses helix. This helix suppression is strong enough for the bi-stability to occur. They also show mono-stability in that they favour one of the two possible switching states. In bi-stable LCDs, mono-stability poses problem only when the less stable state has relaxation time comparable to or shorter than the frame time. Lee et al. explained the high-speed phase modulation using short pitch bistable ferroelectric liquid crystals (LCs) for photonic applications [85].

1.8 DISPERSED LIQUID CRYSTALS

Dispersed liquid crystals have been the subject of occasional study in the literature for many decades. Liquid crystal tactoids were noted in the first half of this century by Zocher and others [86-87]. In 1950's, Frank and Pryce proposed a "spherulite" structure for cholesteric droplets whereas Meyer reported the bipolar droplet structure in 1969 [88-

89]. Phase separation methods of forming dispersed liquid crystal systems exhibiting the dynamic scattering effect were proposed by Taylor [90].

Composites based on LCs have unique electro-optic and magneto-optic properties and novel display applications. Typical examples of these systems are polymer dispersed LCs [91], suspensions of aerosils in LC matrices [92] and magnetic suspensions in LCs [93-94].

In addition to the above, now-a-days, composites based on dispersing nano materials into liquid crystals are getting keen interest due to emerging field of nanotechnology.

1.9 NANO DISPERSED LIQUID CRYSTALS (nDLCs)

Nano-dispersed liquid crystal (nDLC) is a composite material consisting of nano-materials (spherical or rod shaped etc.) dispersed in a liquid crystal matrix either randomly distributed or aligned in the preferred orientation. The knowledge of nano materials has been important to explain their role in producing various modifications in LCs. Depending upon the concentration and properties of nano-particles and LCs, a variety of structures are possible. Because of their composition, nDLCs have very peculiar electro-optical properties. An overview of the developments in the nano dispersed liquid crystals is given in the table 1.1.

Table 1.1: Historical overview of nano dispersed liquid crystals

S. No.	Year	Topics	Contributors
1	2002	The electro-optic properties of colloidal silica filled nematics	Diorio et al. [95]
2	2002	Organisizing carbon nanotubes with liquid crystals	Lynch et al. [96]
3	2002	Effect of dispersed silica particles on the smectic-A-smectic-C* phase transition	Kutnjak et al. [97]
4	2003	Ferroelectric nematic suspension	Reznikov et al. [98]
5	2003	Dielectric relaxation spectroscopy of a nematic liquid crystal doped with ferroelectric $\text{Sn}_2\text{P}_2\text{S}_6$ nanoparticles	Ouskaova et al. [99]
6	2004	Synthesis of novel metal nanoparticles and their application to nano-optical materials	Shiraishi et al. [100]

7	2004	Fingerprint patterning of solid nanoparticles embedded in a cholesteric liquid crystal	Mitov et al. [101]
8	2004	Liquid crystal-carbon nanotube dispersions	Dierking et al. [102]
9	2005	Evidence of Surface Segregation in the Organization of Metallic Nanoparticles Dispersed in a Cholesteric Liquid Crystal	Mitov et al. [103]
10	2005	Controlled Assembly of Gold and Silver Nanoparticles Using Thermotropic Amphiphilic and Conventional Liquid Crystals	Qi et al. [104]
11	2005	Gold-particle-mediated detection of ferroelectric domains on the nanometer scale	Hartling et al. [105]
12	2005	Alignment of nematic liquid crystals using carbon nanotube films	Russell et al. [106]
13	2005	Hierarchical dynamics of nanoparticles in lyotropic lamellar phase	Kimura et al. [107]
14	2005	Electrical-field effect on carbon nanotubes in a twisted nematic liquid crystal cell	Baik et al. [108]
15	2006	Molecular dynamics simulations studies of nanoparticles in an isotropic liquid crystal matrix: Single particle behaviour and pairwise interactions	Tian et al. [109]
16	2006	Imaging of liquid crystals confined in carbon nanotubes	Shah et al. [110]
17	2006	Local deformation of liquid crystal director induced by translational motion of carbon nanotubes under in-plane field	Baik et al. [111]
18	2006	Electrical conductivity and dielectric constant measurements of liquid crystal–gold nanoparticle composites	Prasad et al. [112]
19	2007	Molecular alignment of the 4-octyl-4'-cyanobiphenyl liquid crystal filled with SiO ₂	Ewiss et al. [113]
20	2007	Towards an understanding of nanoparticle- chiral nematic liquid crystal co-assembly	Payne et al. [114]

21	2007	Anchoring a Liquid Crystal Molecule on a Single-Walled Carbon Nanotube	Park et al. [115]
22	2007	Electroactive Superelongation of Carbon Nanotube Aggregates in Liquid Crystal Medium	Jeong et al. [116]
23	2007	Dielectrophoresis force driven dynamics of carbon nanotubes in liquid crystal medium	Srivastava et al. [117]
24	2007	Dynamic response of carbon nanotubes dispersed in nematic liquid crystals	Jeon et al. [118]
25	2007	Unusual double four-lobe textures generated by the motion of carbon nanotubes in a nematic liquid crystal	Jeong et al. [119]
26	2007	Nanoparticles in Liquid Crystals: Synthesis, Self-Assembly, Defect Formation and Potential Applications	Hegmann et al. [120]
27	2007	Effects of carbon nanotubes on electro-optical characteristics of liquid crystal cell driven by in-plane field	Jeon et al. [121]
28	2007	Structure–property relationships in nematic gold nanoparticles	Cseh et al. [122]
29	2007	Enhanced electro-optical properties in gold nanoparticles doped ferroelectric liquid crystals	Kaur et al. [123]
30	2007	Nanoparticles help align liquid crystals	Kuo et al. [124]
31	2008	Nonlinear Liquid Crystal Nano-Metamaterials	Diaz et al. [125]
32	2008	Carbon nanotubes in liquid crystals	Lagerwall et al. [126]
33	2008	Spontaneous macroscopic carbon nanotube alignment via colloidal suspension in hexagonal columnar lyotropic liquid crystals	Scalia et al. [127]
34	2009	Effect of doped insulating nanoparticles on the electro-optical characteristics of nematic liquid crystals	Chen et al. [128]
35	2009	Theory of ferroelectric nanoparticles in nematic liquid crystals.	Lopitana et al. [129]

36	2009	Preparation of ferroelectric nanoparticles and their use in liquid crystalline colloids	Atkuri et al. [130]
37	2009	CdS-nanoparticle-doped liquid crystal displays showing low threshold voltage.	Zhang et al. [131]
38	2009	Photoalignment effect in a liquid-crystal film doped with nanoparticles and azo-dye.	Chen et al. [132]
39	2009	Complementary studies of BaTiO ₃ nanoparticles suspended in a ferroelectric liquid-crystalline mixture	Mikulko et al. [133]
40	2009	Electrooptic and dielectric properties of ferroelectric liquid crystal/single walled carbon nanotubes dispersions confined in thin cells	Podgornov et al. [134]
41	2009	Dielectric and Electro-Optic Properties of New Ferroelectric Liquid Crystalline Mixture Doped with Carbon Nanotubes	Arora et al. [135]
42	2010	The effect of the size of BaTiO ₃ nanoparticles on the electro-optic properties of nematic liquid crystals	Herrington et al. [136]
43	2010	A molecular dynamics study of ferroelectric nanoparticles immersed in a nematic liquid crystal.	Pereira et al. [137]
44	2010	Memory effects in cadmium telluride quantum dots doped ferroelectric liquid crystals	Kumar et al. [138]
45	2010	Enhancing the electro-optical properties of ferroelectric liquid crystals by doping ferroelectric nanoparticles	Liang et al. [139]

1.10 AIM OF THE PRESENT RESEARCH AND FUTURE SCOPE

Besides the technological aspects, nanodispersed LCs are also very promising and interesting from fundamental research point of view. In the recent past, several groups have been succeeded in making nano dispersed liquid crystals (nDLCs) either by dispersing nano materials at high concentration in isotropic solvents or by including nano

materials in lyotropic and thermotropic media. Alignment of nano materials was successfully obtained, but challenges are still faced in particular to obtain materials aligned on large scale for liquid crystalline-nano materials dispersions and to stabilize nano materials in thermotropic liquid crystals. Efforts are still needed to understand the physics, chemistry and materials aspects for better understanding the morphological factors that govern their ordering and hence study their physical properties. Also up to now, a major focus of research is centered on nano dispersed nematic liquid crystals. Very few works has been reported and discussed in the field of nano-dispersed FLCs. The present research work was an attempt to understand the science and nature of interfaces and interactions between some novel ferroelectric liquid crystal (FLC) systems and nano materials of different physical and chemical properties. The objectives for these systems were:

- (1) To prepare nano dispersed liquid crystal composite materials and optimize their physical properties.
- (2) To study the dynamic responses of these systems.
- (3) To characterize these materials for electro-optic, dielectric and thermo-optic properties.

We attempted to understand the dynamic mechanisms after dispersing the SiO_2 , multiwalled carbon nanotubes (MWCNTs), Nickel and C_{60} nano materials into different FLC materials. But however, we face difficulties during dispersion of C_{60} , as they didn't get well dispersed into the FLC matrix which may be due to their heavy mass. The detailed studies were carried out in planer aligned cells to obtain various thermal, dielectric and electro-optic parameters of nDFLC composites. We elaborate the dependence of these properties based upon nature and concentration of nano materials.

REFERENCES

- 1) F. Reintizer, Monatch **9**, 421 (1888).
- 2) O. Lehmann, Zeitschrift fur Physikalische Chemie, **4**, 462 (1889).
- 3) O. Lehmann, Zeitschrift fur Physikalische Chemie, **5**, 427 (1890).
- 4) P. J. Collings, Liquid Crystals: Nature's Delicate Phase of Matter, Princeton University Press (1990).
- 5) P. J. Collings and M. Hird, Introduction to Liquid Crystals: Chemistry and Physics, Taylor and Francis Ltd, (1997).
- 6) P. G. De Gennes, Physics of Liquid Crystals, Oxford University Press (1975).
- 7) S. Chandrasekhar, Liquid Crystal 2nd edn., Cambridge University Press (1992).
- 8) I.C. Khoo, Liquid Crystals: Physical Properties and Non-Linear Optical Phenomenon, John Wiley and Sons Inc. New York (1995).
- 9) G. Freidel, Ann Physique **18**, 273 (1922).
- 10) D. Demus and L. Richter, Textures of Liquid Crystals, Verlag Chemie, New York (1978).
- 11) P.A. Winsor, Chem. Rev. **68**, 1 (1968).
- 12) V. Luzzati and A. Tardieu, Ann. Rev. of Phys. Chem. **25**, 79 (1974).
- 13) Pankaj Kumar, Ph.D. Thesis, Thapar University, Patiala (2007).
- 14) H.S. Kitzerow and C. Bahr, Chirality in Liquid Crystals, Springer (1996).
- 15) P. G. De Gennes and J. Prost, The Physics of Liquid Crystals, 2nd edition, Oxford, Clarendon Press 1973.
- 16) P. Atkins, Physical Chemistry, 7th Edition, Oxford University Press, Oxford (2004).
- 17) J. W. Goodby, J. Mater. Chem. **1**, 307 (1991).
- 18) K.K. Raina, Ph.D. Thesis, Kashmir University (1984).
- 19) E. B. Priestley, P. J. Wojtowicz and P. Sheng, Introduction to Liquid Crystals, Plenum Press, New York (1979).
- 20) R. Williams, adv. Chem. Ser. **44**, 638 (1966).
- 21) R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, J.de Physique **36**, L-69 (1995).
- 22) Vladimir G. Chigrinov, Liquid Crystal Devices: Physics and Applications, Artech House, Boston, London (1999).
- 23) Ernst Lueder, Liquid Crystal Displays, John Wiley & Sons Ltd. (2001).

- 24) O. Hudak, J. Physique **44**, 157 (1983).
- 25) N. A. Clark and S. T. Lagerwall, *Ferroelectric Liquid Crystals*, edited by G. W. Taylor, Vol. **7** of *Ferroelectricity and Related Phenomena*, Gordon and Breach Science, New York (1991).
- 26) Jan P.F. Lagerwall, Ph.D. Thesis, Chalmers University of Technology, Goteborg, Sweden (2000).
- 27) Satyendra Kumar, *Liquid Crystals: Experimental Study of Physical Properties and Phase Transition*, Cambridge University Press (2000).
- 28) Marek Matuszczyk, Ph.D. Thesis, Chalmers University of Technology, Goteborg, Sweden (1996).
- 29) S. Garoff and R.B. Meyer, Phys. Rev. Lett. **38**, 848 (1977).
- 30) J. Valasek, Phys. Rev. **15**, 537 (1920).
- 31) L.A. Bersnav, L.M. Blinov, M.A. Osipov and S.A. Pikin, Mol. Cryst. Liq. Cryst. **158A**, 1(1988).
- 32) J. Funfschilling, Condensed Matter News, **1**, 12 (1991).
- 33) R. Blinc, Condensed Matter News **1**, 17 (1991).
- 34) J.W. Goodby, Mol. Cryst. Liq. Cryst. **292**, 245 (1997).
- 35) P.M. Chaikin and T.C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge University Press (1998).
- 36) J.K. Ahuja, Ph.D. Thesis, Thapar Institute of Engineering and Technology, Patiala (2000).
- 37) *Liquid Crystals and Polymer Systems*, Merck Industrial Chemicals, LICRILITE.
- 38) Data Sheet, BDH, UK, Hoffman La Roche, Switzerland.
- 39) A. Yoshizawa, I. Nishiyama, M. Fukumasa, T. Hirai and M. Yamane, Jap. J. Appl. Phys. **28**, L1269 (1989).
- 40) S. Wrobel, W. Haase, M. Pfeiffer, L. Beresnev and T. Geelhaar, Mol. Cryst. Liq. Cryst. **212**, 335 (1992).
- 41) M. Kasper, H. Sverenyak, V. Hamplova, S.A. Pakhomov and M. Glogarova, Mol. Cryst. Liq. Cryst. **260**, 241 (1995).
- 42) Sven Owe Vallerien, Rudolf Zental, Friedrich Kremer, Heinrich Kapitza and Erhard W. Fischer, Macromol. Chem. **10**, 333 (1989).
- 43) B. Fischer, C. Thieme, T.M. Fischer, F. Kremer, T. Oge and R. Zental, Liq. Cryst. **22**, 65 (1997).

- 44) H. Poths, E. Wischhoff, R. Zentel, A. Schonfeld, G. Henn And F. Kremmer, Liq. Cryst. **18**, 811 (1995).
- 45) I. Alig, D. Braun, M. Jarek and G.P. Hellman, Macromol. Symp. **90**, 173 (1995).
- 46) J.C. Dubois, Physica Scripta **T23**, 299 (1988).
- 47) S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, Pramana **9**, 471 (1977).
- 48) A. Jakali, A. Saupe, G. Scherowsky and Xin Hua Chen, Liq. Cryst. **22**, 309 (1997).
- 49) N. Boden, R.J. Buschby and Andrew N. Commidge, Liq. Cryst. **25**, 47 (1998).
- 50) M. Baron and R. F. T. Stepto, Pure Appl. Chem. **74**, 493 (2002).
- 51) S. Chandrasekhar and G. S. Ranganath, Rep. Prog. Phys. **53**, 57 (1990).
- 52) H. Bock and W. Helfrich, Liq. Cryst. **12**, 697 (1997).
- 53) G. Heppke, D. Krueke, M. Muller and H. Bock, Ferroelectrics **179**, 203 (1997).
- 54) T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, J. Mater. Chem. **6**, 1231 (1996).
- 55) Chong-Kwang Lee, A. Primak, A. Jakali, E.-Joon Choi, Wang-Cheol Zin and Liang-Chy Chien, Liq. Cryst. **28**, 1293 (2001).
- 56) D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Körblöva and D. M. Walba, *Science* **278**, 1924 (1997).
- 57) T. Sekine, T. Niori, M.Sone, J. Watanabe, S.W. Choi, Y. Takanishi and H. Takezoe, Jap. J. Appl. Phys. **36**, 6455 (1997).
- 58) T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S.W. Choi and H. Takezoe, J. Mater. Chem. **7**, 1307 (1997).
- 59) Y. Matsunaga S. Miyamoto, *Mol. Cryst. Liq. Cryst.* **237**, 311 (1993).
- 60) J. Watanabe, *Workshop on banana liquid crystals: chirality by Achiral Molecules*, Berlin (1997).
- 61) J. Watanabe, T. Niori, S.-W. Choi, Y. Takanishi and H. Takezoe, *Jpn. J. appl. Phys.* **37**, L401-L403 (1998).
- 62) B. Senyuk, A presentation on *Liquid crystals: a simple view on a complex matter*, Liquid Crystal Institute, Kent State University, USA.
- 63) S.V. Shilov, H. Skupin, F. Kremmer, T. Witting and R. Zentle, Physical Review Letters **79**, 1686 (1997).
- 64) D. Coates, W.A. Crossland, J.H. Morrissy and B. Needham, J. Phys. D App. Phys. **11**, 2025 (1978).

- 65) A. Hohmuth, B. Schiewe, S. Heinemann and H. Kresse, *Liq. Cryst.* **22**, 211 (1986).
- 66) R. Simsons and H.J. Coles, *Liq. Cryst.* **1**, 281 (1986).
- 67) Samruti Khosla, K.K. Raina and H.J. Coles, *Curr. Appl. Phys.* **3**, 135 (2003).
- 68) M.I. Elhaz, A. Skoulios, D.G. J. Newton, P. Hodge and H. J. Coles, *Liq. Cryst.* **19**, 373 (1993).
- 69) Corrie T. Imrie and Geoffery R. Luckhurst, *J. Mater. Chem.* **8**, 1339 (1998).
- 70) Atsushi Yoshizawa, *Journal of Materials Chemistry*, **18**, 2877 (2008).
- 71) N. A. Clark and S.T. Lagerwall, *App. Phys. Lett.* **36**, 899 (1980).
- 72) S. S. Bawa, Kanchan Sexena and Subhas Chandra, *Jap. J. Appl. Phys.* **28**, 662 (1989).
- 73) M. Schadt, *Display Technologies and Applications* **13**, **11** (1992).
- 74) A. Jakali and A. Saupe, *Phy. Rev. A* **45**, 5674 (1992).
- 75) Ingo Dierking, *J. Phys.: Condens. Matter* **17**, 4403 (2005).
- 76) I. Dahl, S.T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
- 77) N.A. Clark, M.A. Handschy and S. T. Lagerwall, *Mol. Cryst. Liq. Cryst.* **94**, 213 (1983).
- 78) I.C. Khoo and S.T. Wu, *Optics and Non-Linear Optics of Liquid Crystals*, Singapore: World Scientific (1993).
- 79) L.A. Bersnav, V. G. Chigrinov, D. I. Drgachev, E.P. Polishdaev, J. Funfschilling and M. Schadt, *Liq. Cryst.* **5**, 1171 (1989).
- 80) J. Funfschilling and M. Schadt, *J. App. Phys.* **66**, 3877 (1989).
- 81) Samruti Khosla, Nitin Sood, K.K. Raina and S.S. Bawa, *Mol. Cryst. Liq. Cryst.* **524**, 119 (2010).
- 82) J. Funfschilling and M. Schadt, *Jap. J. App. Phys.* **35**, 5765 (1996).
- 83) A Jakali, L. Bata, L.A. Bersnev, *Mol. Cryst. Liq. Cryst.* **177**, 43 (1989).
- 84) J. Funfschilling and M. Schadt, *Jap. J. App. Phys.* **30**, 741 (1991).
- 85) Ju-Hyun Lee, Dong-Woo Kim, Yung-Hsun Wu, Chang-Jae Yu, Sin-Doo Lee, and Shin-Tson Wu, *OPTICS EXPRESS* **13**, 7732 (2005).
- 86) H. Zocher, *Z. anorg. Chem.* **147**, 91-110 (1925).
- 87) J.D.Bernal and I. Fankuchen, *J. Gen. Physiol.* **25**, 11-165 (1941).
- 88) R. Robinson, J. C. Ward, and R.B. Beevers, Part 2. *Trans. Faraday Soc.*, **54**, 29-42 (1958).
- 89) R. B. Meyer, *Phys. Rev. Lett.* **22**, 918-21 (1969).

- 90) L. J. Taylor, US Patent 4, **101**, 207 (1978).
- 91) J. W. Doane, N.A. Wu, B.G Vaz. And S. Zumer, Appl. Phys. Lett. **48**, 269. (1986).
- 92) M. Kreuzer, T. Tschudi and R. Eidenschink, Appl. Phys. Lett. **62**, 1712 (1993).
- 93) F. Brochard and P.G. De Gennes, J. Phys. **31**, 691(1970).
- 94) B. J. Liang and S.H. Chen, Phys. Rev. A **39**, 1441 (1989).
- 95) N. J. Diorio, Jr., M.R. Fisch and J.W. West, Liq. Cryst. **29**, 589 (2002).
- 96) Michael D. Lynch and David L. Patrick, Nano Letters **2**, 1197 (2002).
- 97) Z. Kutnjak, S. Kralj and S. Zume, Phys. Rev. E **66**, 041702 (2002).
- 98) Yurii Reznikov, Olexander Buchnev, Olexander Tereshchenko, Victor Reshetnyak, Anatoliy Glushchenko and John Westa, Appl. Phys. Lett. **82**, 1917 (2003).
- 99) E. Ouskaova, O Buchnev, V Reshetnyak, Yu. Reznikov and H. Kresse, Liq. Cryst. **30**, 1235 (2003).
- 100) Yukihide Shiraishi, Japan Nanonet Bulletin (2004).
- 101) Michel Mitov, Christian Bourgerette and Francois de Guerville, J. Phys. Condens. Matter **16**, S1981 (2004).
- 102) I. Dierking, G. Scalia, P. Morales, J. of Appl. Phys. **97**, 044339 (2005).
- 103) Michel Mitov, Francois de Guerville and Christian Bourgerette, Mol.Cryst. Liq. Cryst. **435**, 13/[673] (2005).
- 104) Hao Qi, Piaopiao Wei, Nadezhda Sertova, and Torsten Hegmann, Proceedings of 5th IEEE Conference on Nanotechnology, Japan (2005).
- 105) Thomas Härtling and Lukas M. Eng, Appl. Phys. Lett. **87**, 142902 (2005).
- 106) Joette M. Russell, Soojin Oh, Issac LaRue, Otto Zhou, Edward T. Samulski, Thin Solid Films **509**, 53 (2006).
- 107) Yasuyuki Kimura, Teppei Mori, Akira Yamamoto, Daisuke Mizuno, Mol.Cryst. Liq. Cryst. **435**, 51 (2005).
- 108) In-Su Baik, Sang Youn Jeon, and Seung Hee Lee, Kyung Ah Park, Seok Ho Jeong, Kay Hyeok An, and Young Hee Lee, Appl. Phys. Lett. **87**, 263110 (2005).
- 109) Pu Tian and Grant D. Smith, Matthew Glaser, J. Chem. Phys. **124**, 1611101(2006).
- 110) Hemang J. Shah and Adam K. Fontecchio, Maria Pia Rossi, Davide Mattia, and Yury Gogotsi, Appl. Phys. Lett. **89**, 043123 (2006).

- 111) In-Su Baik, Sang Yeon Jeon, Seok Jin Jeong, and Seung Hee Lee, Kay Hyeok An, Seok Ho Jeong, and Young Hee Lee, *J. Appl. Phys.***100**, 074306 (2006).
- 112) S. Krishna Prasad, K. L. Sandhya, Geetha G. Nair, Uma S. Hiremath, C. V. Yelamaggad, S. Sampath, *Liq. Cryst.* **33**, 1121(2006).
- 113) M. A. Zaki Ewiss, F. Moawia, B. Stoll, *Liq. Cryst.* **34**, 127 (2007).
- 114) J.C. Payne, E.L. Thomas, *Advanced Functional Materials* **17**, 2717 (2007).
- 115) Kyung Ah Park, Seung Mi Lee, Seung Hee Lee, and Young Hee Lee, *J. Phys. Chem. C* **111**, 1620 (2007).
- 116) Seok Jin Jeong, Kyung Ah Park, Seok Ho Jeong, Hee Jin Jeong, Kay Hyeok An, Chang Woon Nah, Didier Pribat, Seung Hee Lee, and Young Hee Lee, Sr., *Nano Letters*, 0, A-E (2007).
- 117) Anoop Kumar Srivastava, Seok Jin Jeong, Myong-Hoon Lee, and Seung Hee Lee, Seok Ho Jeong and Young Hee Lee, *J. Appl. Phys.* **102**, 043503 (2007).
- 118) Sang Youn Jeon, Kyung Ah Park, In-Su Bai, Seok Jin Jeong, Seok Ho Jeong, Kay Hyeok An, Seung Hee Lee, and Young Hee Lee, *Nano: Brief Reports and Reviews* **2**, 41(2007).
- 119) Seok Jin Jeong, Palanivelu Sureshkumar, Kwang-Un Jeong, Anoop K. Srivastava, Seung Hee Lee, Seok Ho Jeong, Young Hee Lee, Ruibo Lu, and Shin-Tson Wu, *Optics Express* **15**, 11698 (2007).
- 120) Torsten Hegmann, Hao Qi and Vanessa M. Marx, *Journal of Inorganic and Organometallic Polymers and Materials* **17**, 483(2007).
- 121) Sang Youn Jeon, Seung Hwan Shin, Seok Jin Jeong, and Seung Hee Lee, Seok Ho Jeong and Young Hee Lee, Hyun Chul Choi and Kyeong Jin Kim, *Appl. Phy. Lett.* **90**, 121901(2007).
- 122) Liliana Cseh and Georg H. Mehl, *J. Mater. Chem.* **17**, 311(2007).
- 123) S. Kaur, S. P. Singh, and A. M. Biradar, Amit Choudhary and K. Sreenivas, *Appl. Phy. Lett.* **91**, 023120 (2007).
- 124) Chia-Wei Kuo, Shie-Chang Jeng, Hsing-Lung Wang, and Chi-Chang Liao, *Appl. Phy. Lett.* **91**, 141103 (2007).
- 125) A. Diaz, S. Kubo, D.H. Kwon, J. Park, D. Werner, T. Mallouk and I.C. Khoo, *IEEE*, 978-1-4244-1595-3/08 (2008).
- 126) Jan P. F. Lagerwall and Giusy Scalia, *J. Mater. Chem.***18**, 2890–2898 (2008).
- 127) Giusy Scalia, Clemens von Buhler, Constanze Hagele, Siegmund Roth, Frank Giesselmann and Jan P. F. Lagerwall, *Soft Matter* **4**, 570–576 (2008).

- 128) W-T. Chen, P.-S. Chen and C.-Y. Chao, *Jap. J. Appl. Phys.* **48**, 015006 (2009).
- 129) L. M. Lopitana and J. V. Selinger, *Phy. Rev. Lett.* **102**, 197802 (2009).
- 130) H. Atkuri, G. Cook, D.R. Evans, C-I Cheon, A. Glushchenko, V. Reshetnyak, Yu Reznikov, J. West and K. Zhang, *J. Opt. A: Pure Appl. Opt.* **11**, 024006 (2009).
- 131) Tianyi Zhang, C. Zhong and J. Xu, *Jap. J. Appl. Phys.* **48**, 055002 (2009).
- 132) Wen Zheng Chen, Yi-T. Tsai and T.-H. Lin, *Appl. Phys. Lett.* **94**, 201114 (2009).
- 133) A. Mikulko, P. Arora, A. Glushchenko, A. Lapanik and W. Haase, *EPL* **87**, 27009 (2009).
- 134) Fedor V. Podgornov, Anastasia M. Suvorova, Artsiom V. Lapanik and Wolfgang Haase, *Chemical Physics Letters* **479**, 206-210 (2009).
- 135) P.Arora, A. Mikulko, F. Podgornov and W. Hasse, *Mol. Cryst. Liq. Cryst.* **502**, 1-8 (2009).
- 136) M. R. Herrington, O. Buchnev, M. Kaczmarek and I. Nandhakumar, *Mol.Cryst.Liq. Cryst.* **527**, 72[228] (2010).
- 137) M.S.S. Pereira, A. A. Canabarro, I. N. Oliveira, M.L. Lyra and L.V. Mirantsev, *Eup. Phys. J. E* **31**, 81 (2010).
- 138) A.Kumar, J. Prakash, M. T. Khan, S.K. Dhawan and A. M. Biradar, *Appl. Phys. Lett.* **97**, 163113 (2010).
- 139) Hao-Hsun Liang, Ya-Zhi Xiao, Fu-Jhen Hsh, Che-Cheng Wu and Jiunn-Yih Lee, *Liq. Cryst.* **37** (2010) 255–261.

CHAPTER 2

Theoretical Considerations for Ferroelectric Liquid Crystals

Overview

This chapter includes the basic dielectric and electro-optic relaxations present in the LCs. The collective motion in SmC phase mainly consist of four modes which are described by using dielectric spectroscopy. A review of the non-collective re-orientation mechanisms, which are common to all liquid crystals and the collective polarization mechanisms in the smectic C* phase of liquid crystals has been discussed. Theory of electro-optic transmission and contrast is also given at the end of the chapter.*

2.1 DIELECTRIC RELAXATIONS

Liquid crystals materials are dielectric materials. Dielectrics possess low electrical conductivity but polarize in the presence of field [1-6]. The electric field ‘E’ induces a polarization in these materials. The magnitude and direction of polarization is a characteristic of the material and is related to dielectric susceptibility ‘ χ ’ by

$$P = \chi \epsilon_0 E \quad (2.1)$$

where, ϵ_0 is the permittivity of free space and susceptibility is related to relative permittivity ϵ_r by the following relation

$$\chi = \epsilon_r - 1 \quad (2.2)$$

Thus eq. 2.1 becomes

$$P = (\epsilon_r - 1) \epsilon_0 E \quad (2.3)$$

Hence, permittivity relates electric field with the macroscopic polarization. This macroscopic polarization is a result of microscopic polarizations, which are divided into two main categories: charge displacement polarization and orientational polarization. In the former case dipole moment is induced due to displacement of the charges. This process is very fast and contributes to ϵ_r at very high frequencies. In the second case, with the application of an electric field, the aligning force opposes the thermal disorder of the permanent dipole and we will get a bias in the molecular vibration and rotation corresponding to partial orientation of the dipoles, which gives a contribution to the permittivity.

If a sufficiently strong electric field is applied over a ferroelectric material, the spontaneous polarization will line up with the field and as a result, such materials have large permittivity. This is known as non-collective molecular re-orientation process. This

dipole moment may also collective i.e. a large no. of molecules move in phase with each other. All mechanisms will be present in the presence of DC field, but for an AC field, contribution from each mechanism will eventually disappear when the frequency is varied. It is driven back and forth at too high frequency; it will not have time to be activated before the driving field changes sign. Thus at higher frequencies, there will be no contribution to the permittivity. On approaching a certain characteristic frequency, the driven motion seriously begin to lag behind the force. At this frequency, the polarization is 90° out of phase with E. The fluctuation amplitude has been decreased to half of its maximum value and at this point maximum energy is absorbed from the electric field and transformed into heat of the material.

In nematics, there are two modes of orientational polarization and in SmA* there is one collective mode known as an electro clinic or soft mode (SM). In SmC* phase, we have a strong mode that give contribution to ϵ from the important polarization of each layer which tries to align in the direction of field by easy azimuthal motion around the smectic cones. This mode is often called goldstone mode (GM). The polarization mechanisms possible in liquid crystals are described in the table 2.1 [1]. The charge displacement and polarization modes due to their high frequencies could not be studied due to their experimental limitations.

Table 2.1 Possible polarization mechanisms in liquid crystals

Mechanism	Type	Method to Study
Electronic polarization	Induced dipole	UV/VIS-absorption spectroscopy
Non-Collective orientational polarization	Permanent dipoles align	Dielectric spectroscopy, IR absorption spectroscopy
Collective orientational (Ferro-electric) polarization	Permanently aligned dipole reoriented	Dielectric spectroscopy

2.1.1 Debye type relaxation

With the application of an electric field, the polarization of the medium approaches its equilibrium value exponentially with a characteristic time constant τ .

$$P = P_f (1 - e^{-t/\tau}) \quad (2.4)$$

where P_f is the saturation value of polarization. If the field is switched off, the polarization will decay according to the relation

$$P = P_f e^{-t/\tau} \quad (2.5)$$

The Debye function is defined as

$$\alpha(t) \propto \exp(-t/\tau) \quad (2.6)$$

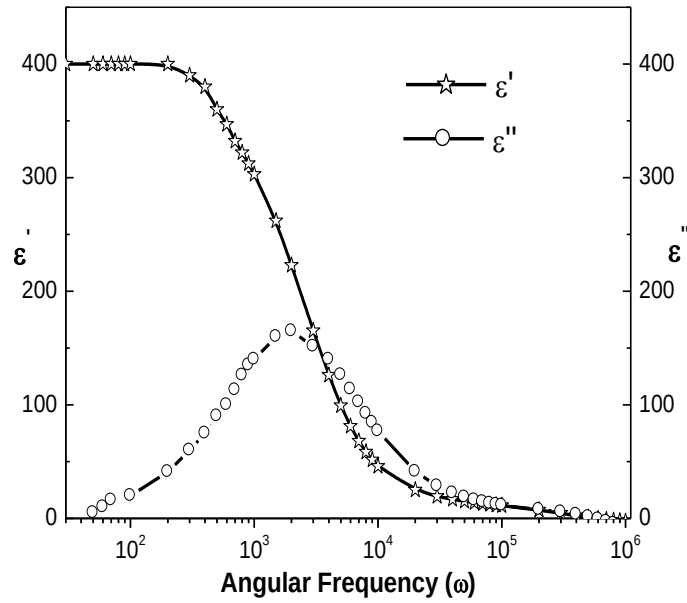


Figure 2.1 The simple Debye type relaxation behaviour of real and imaginary parts of permittivity [1].

where τ is the relaxation time that depends upon the temperature but independent of time. In the presence of an AC field, the response of the material changes as a function of frequency and temperature. Assuming that relaxation behavior of each mode is characterized by one single relaxation frequency; the complex dielectric permittivity can be written as

$$\varepsilon^*(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T) \quad (2.7)$$

where $\omega = 2\pi f$ is the angular frequency of the applied field and T is the temperature of the system. $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$ are respectively the real and imaginary parts of dielectric permittivity. It may also be written as

$$\varepsilon^*(\omega, T) = \frac{\Delta\varepsilon_r(T)}{1 + i\omega\tau_r} + \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau_r} + \varepsilon_\infty \quad (2.8)$$

$$\text{where } \Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty \quad (2.9)$$

is the dielectric strength of the material and ϵ_o and ϵ_∞ are the static and infinite frequency dielectric permittivity respectively. τ_r is the relaxation time of the corresponding mode. The separate real and imaginary parts may be written as

$$\epsilon'(\omega) = \epsilon_\infty + \frac{\epsilon_o - \epsilon_\infty}{1 + \omega^2 \tau^2}$$

$$(2.10) \epsilon''(\omega) = \omega \tau \frac{\epsilon_o - \epsilon_\infty}{1 + \omega^2 \tau^2}$$

$$(2.11)$$

ϵ'' is also known as dielectric loss factor. D is the dissipation factor which is given by

$$D = \frac{\epsilon''(\omega)}{\epsilon'(\omega)} \quad (2.12)$$

Eqns.2.10 and 2.11 are called Debye equations and this type of relaxation is called Debye relaxation. The generalization of Debye formulation describes a dielectric distribution of relaxation times associated with a single dielectric process. The plots of these equations are shown fig. 2.1[1]. If we sweep the frequency from zero to infinity it is seen from the equation that ϵ' has practically constant value till frequency approaches to relaxation frequency. It then decreases having an inflexion point at $\omega\tau = 1$ and becomes zero for $\omega\tau > 1$. ϵ'' is vanishingly small except in neighborhood for $\omega\tau = 1$, where it has maximum value. This is where absorption occurs. In terms of frequency domain Debye equation is written as

$$\epsilon'(\omega) = \epsilon_\infty + \frac{\epsilon_o - \epsilon_\infty}{1 + \left(\frac{f}{f_r}\right)^2} \quad (2.13)$$

$$\epsilon''(\omega) = \frac{f}{f_r} \frac{\epsilon_o - \epsilon_\infty}{1 + \left(\frac{f}{f_r}\right)^2} \quad (2.14)$$

By successively increasing the frequency of measuring field, the real part of permittivity decreases stepwise; (fig.2.2), each time the frequency passes the relaxation frequency. The difference between the low and high frequency contributions of the mode to the total dielectric constant is called the dielectric strength of the mode. If several modes influence our experiment, we get several ϵ' and f_r values, each corresponding to one contributing mechanism. Each mode will then also get its specific set of ϵ_o and ϵ_∞

dielectric strength i.e. the maximum contribution of the mode to the real part of the dielectric permittivity.

2.1.2 Non-Debye relaxation

When applying the Debye results to actual experimental data, one soon realizes that the Debye equation seldom works. For polymer systems and in many cases also in low molar mass liquid crystals, a mode turns out to be characterized by the distribution of relaxation time and therefore it is impossible to obtain a good fit of eqn. (2.13) and eqn. (2.14) to experimental data. In order to cope with this problem, the above results will have to be modified. Such a modification was first introduced by KS Coles and RH Coles, in 1941 and their starting expression bears the name Cole-Cole equation.

$$\varepsilon^*(\omega, T) = \frac{\Delta\varepsilon_i(T)}{1 + (i\omega\tau_r)^{(1-\alpha)}} + \varepsilon_\infty = \frac{\varepsilon_o - \varepsilon_\infty}{1 + i\left(\frac{f}{f_r}\right)^{(1-\alpha)}} + \varepsilon_\infty \quad (2.15)$$

Where α is the distribution parameter i.e. spreading factor for a particular re-orientation process. For $\alpha = 0$ the above expression is equivalent to eqn. 2.8, considering that $\omega\tau = 1$ or $f/f_r = 1$. Separating into real and imaginary components we get the following expressions.

$$\varepsilon'(\omega, T) = \varepsilon_\infty + \Delta\varepsilon_i(T) \frac{1 + \left(\frac{f}{f_r}\right)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right)}{1 + 2\left(\frac{f}{f_r}\right)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) + \left(\frac{f}{f_r}\right)^{2(1-\alpha)}} \quad (2.16)$$

$$\varepsilon''(\omega, T) = \varepsilon_\infty + \Delta\varepsilon_i(T) \frac{\left(\frac{f}{f_r}\right)^{1-\alpha} \cos\left(\frac{\alpha\pi}{2}\right)}{1 + 2\left(\frac{f}{f_r}\right)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) + \left(\frac{f}{f_r}\right)^{2(1-\alpha)}} \quad (2.17)$$

The above equations can also be written as

$$\varepsilon' - \varepsilon_\infty = \frac{1}{2}(\varepsilon_o - \varepsilon_\infty) \left[\frac{\sinh((1-\alpha)\ln\omega\tau_o)}{\cosh[(1-\alpha)\ln\omega\tau_o] + \sin\frac{1}{2}\pi\alpha} \right] \quad (2.18)$$

$$\varepsilon'' = \frac{1}{2}(\varepsilon_o - \varepsilon_\infty) \left[\frac{\cosh \frac{1}{2} \pi \alpha_o}{\cosh[(1-\alpha) \ln \omega \tau_o] + \sin \frac{1}{2} \pi \alpha} \right] \quad (2.19)$$

when $\alpha=0$, the Cole-Cole equation reduces to the previous Debye expression, but for non-zero values of α we get distribution of relaxation time, which in the dispersion plot gives less distinct peak and in the absorption plot results in the broader and flatter peak. The value of α can vary from zero to one.

By eliminating the frequency in the Debye equation one gets the equation of circle. This is the basis for a very illustrative way of presenting the experimental permittivity data. The parameter α is purely empirical and there is no microscopic theory for it. If we imagine a certain dipole being in a liquid crystal containing only one single molecular species, we will find a pure Debye behaviour. Very often, however we are investigating the multi-component behaviour in which each particular dipole would not have a unique environment. This would lead to smear out of the relaxation process and α is not equal to zero. In polymers, the environment is even much more complex and varying and we get large value of α (up to 0.9).

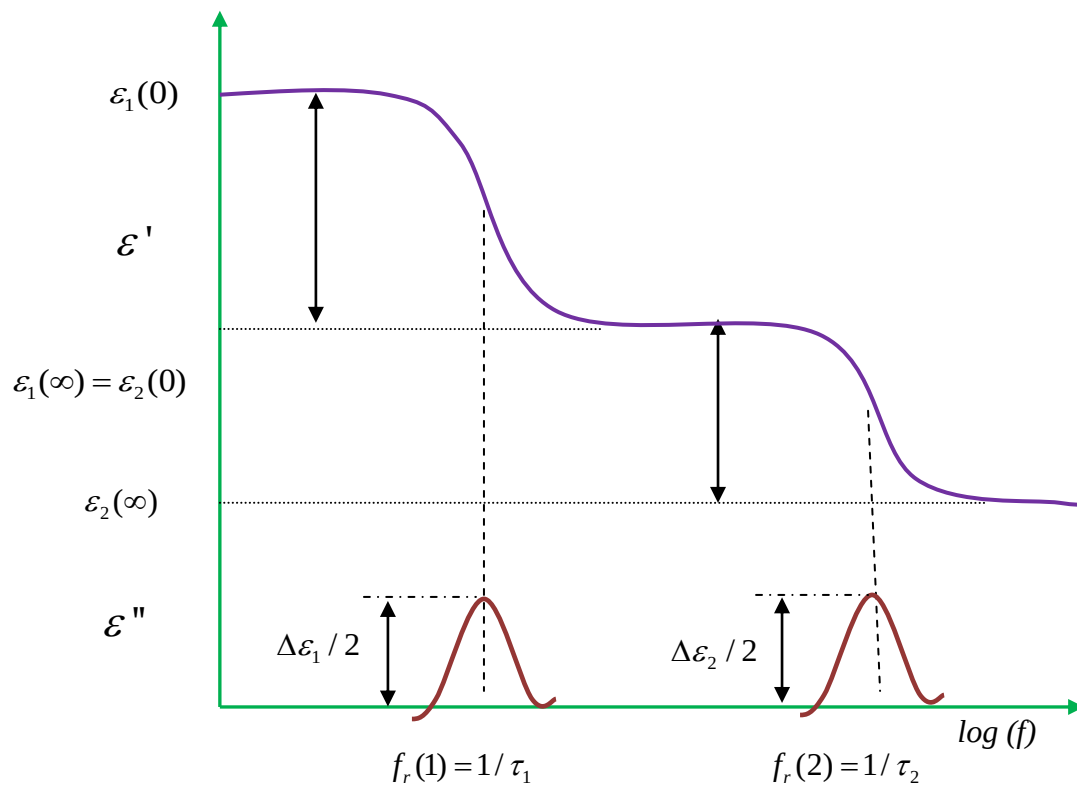


Figure 2.2 Different relaxations present in the materials with a range of frequencies represented in the form of variation real and imaginary part of permittivity [1].

2.1.3 Cole-Cole plots

By eliminating the frequency from the equation (2.13) and (2.14), we get the following expression

$$\left(\varepsilon - \left(\varepsilon_{\infty} + \frac{\Delta\varepsilon}{2} \right) \right)^2 + (\varepsilon'')^2 = \left(\frac{\Delta\varepsilon}{2} \right)^2 \quad (2.20)$$

This is an equation of the circle centered on the point $\varepsilon' = \varepsilon_{\infty} + \Delta\varepsilon/2$, $\varepsilon'' = 0$ and a Debye type process should therefore produce a semicircle if ε'' is plotted against ε' , fig.2.3 (a). This type of plot is known as Cole-Cole plot. Much qualitative information can be gathered from this type of representation of data. Since maximum absorption occurs at relaxation frequency, the top of the semicircle corresponds to this frequency.

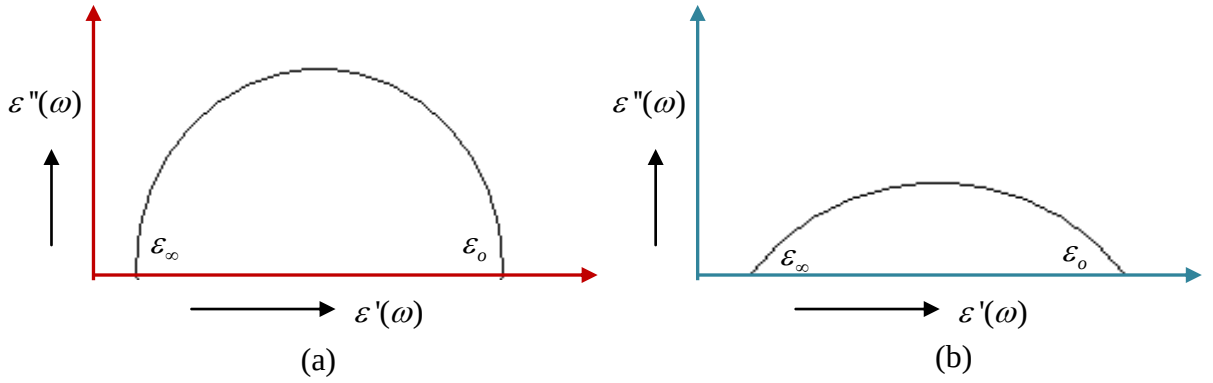


Figure 2.3 Cole-Cole plots for a Debye dielectric relaxation [6].

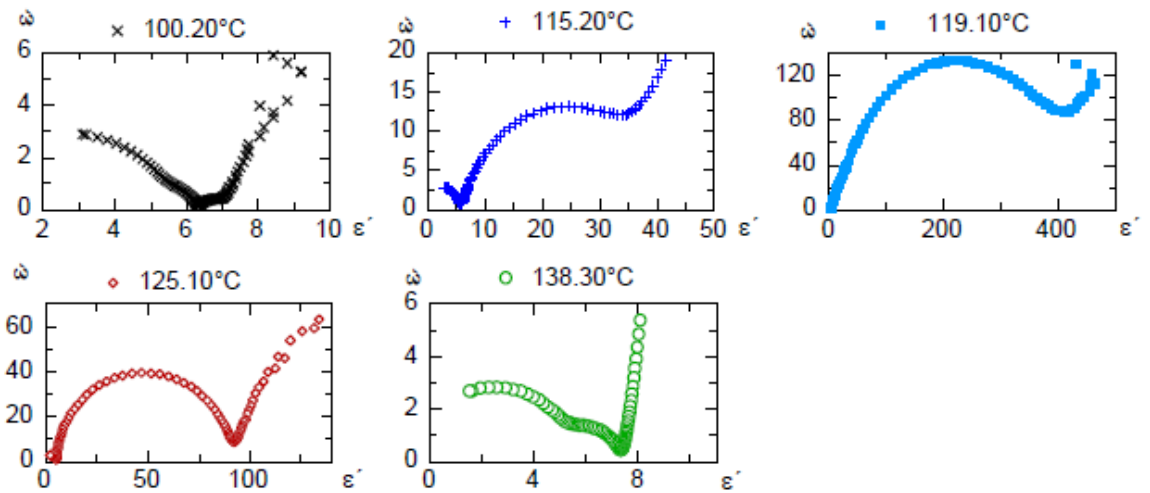


Figure 2.4 Cole-Cole plots showing the overlapping of modes at different temperatures for CG50 data. These are complex and show deviation from pure Debye behavior [1].

However, as discussed earlier, the real polarization mechanisms are often characterized by a distribution of relaxation time and in order to tackle this behavior, Cole and Cole proposed equation (2.13). If we eliminate frequency from equations (2.14) and (2.15), again the equation of circle is obtained but with some important difference in relation to Debye case.

$$\left(\varepsilon' - \left(\varepsilon_{\infty} + \frac{\Delta\varepsilon}{2} \right) \right)^2 + \left(\varepsilon'' + \frac{\Delta\varepsilon}{2} \tan\left(\frac{\alpha\pi}{2}\right) \right)^2 = \left(\frac{\Delta\varepsilon}{2 \cos\left(\frac{\alpha\pi}{2}\right)} \right)^2 \quad (2.21)$$

The radius of the circle has now grown by a factor $1/\cos(\alpha\pi/2)$ and the center has moved to $\Delta\varepsilon \tan(\alpha\pi/2)$ below the ε' axis. Thus the permittivity data from a distributed mode will produce an arch with an opening angle less than 180° as shown in fig. 2.3(b). If we can locate the center of the circle, we can determine the value of α . Debye type and Non-Debye relaxations are best visualized by Cole-Cole plots as shown in fig. 2.3 (a, b) respectively.

When plotting the real experimental data one often encounter the problem of partially overlapping modes. The shape of Cole-Cole plot changes as shown in the fig. 2.4 for the cases where relative frequencies of the modes can't be determined easily [1].

2.2 DIELECTRIC RELAXATIONS IN LOW MOLAR MASS LIQUID CRYSTALS

Both collective and non-collective relaxations are expected in liquid crystalline materials. Collective relaxation involves the coherent motion of a large number of molecules, while the non-collective relaxations are related to non-correlated motion. The easily observable change in the two fluctuation types is that the collective processes being related to a macroscopic configurational change will lead to change in the optical properties of the sample while non-collective will not.

2.2.1 Collective polarization mechanism in chiral smectic phases

In spite of long range nematic order, no collective mode of this phase can however be excited in dielectric spectroscopy due to quadrupole character of the nematic order. The same is also valid for the non-chiral smectic phases.

Ferroelectric liquid crystals (FLCs) are usually chiral smectic (SmC^*) systems but some banana shaped liquid crystals show ferroelectricity even in the absence of chirality.

Dielectric relaxation takes place in the SmA* and SmC* phases due to the fluctuation of the molecular tilt and polarization [7-21].

In SmC* phase, the chirality of molecules breaks the mirror symmetry with respect to the plane of tilt and normal to the smectic layers. Therefore, a transverse spontaneous polarization is induced locally, which is perpendicular to the tilt direction and normal to the layers. The molecules within one layer are tilted uniformly but the direction of tilt processes helicoidally as one goes from one smectic layer to another. Together with the tilt, the transverse electric polarization of such a helicoidal structure is equal to zero but the systems are nevertheless called ferroelectrics because of the existence of a local spontaneous polarization and because of their characteristic behavior in the electric fields [22-26].

Application of an electric field of magnitude E parallel to the smectic layers disturbs the helix in such a way that an average macroscopic polarization $\langle P_i \rangle$ is induced. It also influences the molecular tilt. So, the dielectric relaxation in these systems is due to the disturbance of order parameters by the electric field. This disturbance can be divided into two parts

- (i) Amplitude Changes (change in magnitude of tilt θ_0 and polarization P_i)
- (ii) Phase changes (changes in the direction of tilt and the polarization)

Hence dielectric response of the system will consist of four directly active type of fluctuations (apart from the high frequency electronic response): one amplitude (amplitude mode) and one orientational (Plasmon mode) connected to each order parameter, ξ and P . The two connected to the fluctuation of polarization order parameter have relaxation frequency of the order of 500MHz. The other two are connected to relaxation of the director fluctuation and are of low frequency [27-31].

In SmA* phase the phason are degenerate with amplitude (instead of amplitude fluctuation along $\hat{r} = \sqrt{\hat{x}^2 + \hat{y}^2}$ and orientational fluctuation along $\hat{\phi}$, we have amplitude fluctuation along x-axis and y-axis). It is due to the homogeneous arrangement of the molecules in the layers. Thus here we should only be able to observe two modes. As all modes are related to the polarization, they should be observed with the measuring field applied along the smectic layers i.e. in planer geometry. Denoting the amplitude changes by $\delta\theta_1$ and δP_1 and the phase changes by $\delta\theta_2$ and δP_2 [fig. 2.5(a, b, c)], we can express order parameter as [23-26]

$$\begin{cases}
\xi_1(t) = \theta_o \cos(qZ) + \delta\theta_1(t) \cos(qZ) - \delta\theta_2(t) \sin(qZ) \\
\xi_2(t) = \theta_o \cos(qZ) + \delta\theta_1(t) \sin(qZ) - \delta\theta_2(t) \cos(qZ) \\
P_x(t) = -P_o \sin(qZ) + \delta P_1(t) \sin(qZ) - \delta\theta_2(t) \cos(qZ) \\
P_y(t) = -P_o \cos(qZ) + \delta P_1(t) \cos(qZ) - \delta P_2(t) \sin(qZ)
\end{cases} \quad (2.22)$$

Linear combinations of the amplitude changes of the order parameters are denoted as the soft mode (SM) and linear combination of the phase changes of the order parameters are denoted as the goldstone mode (GM). The modes due to director orientation are commonly denoted by SM and the GM whereas the modes connected to polarization reorientation are known as polarization soft mode (PSM) and the polarization goldstone mode (PGM). Thus in general, SM can be identified as the response connected to the amplitude changes and GM is response connected with the phase change of order parameters.

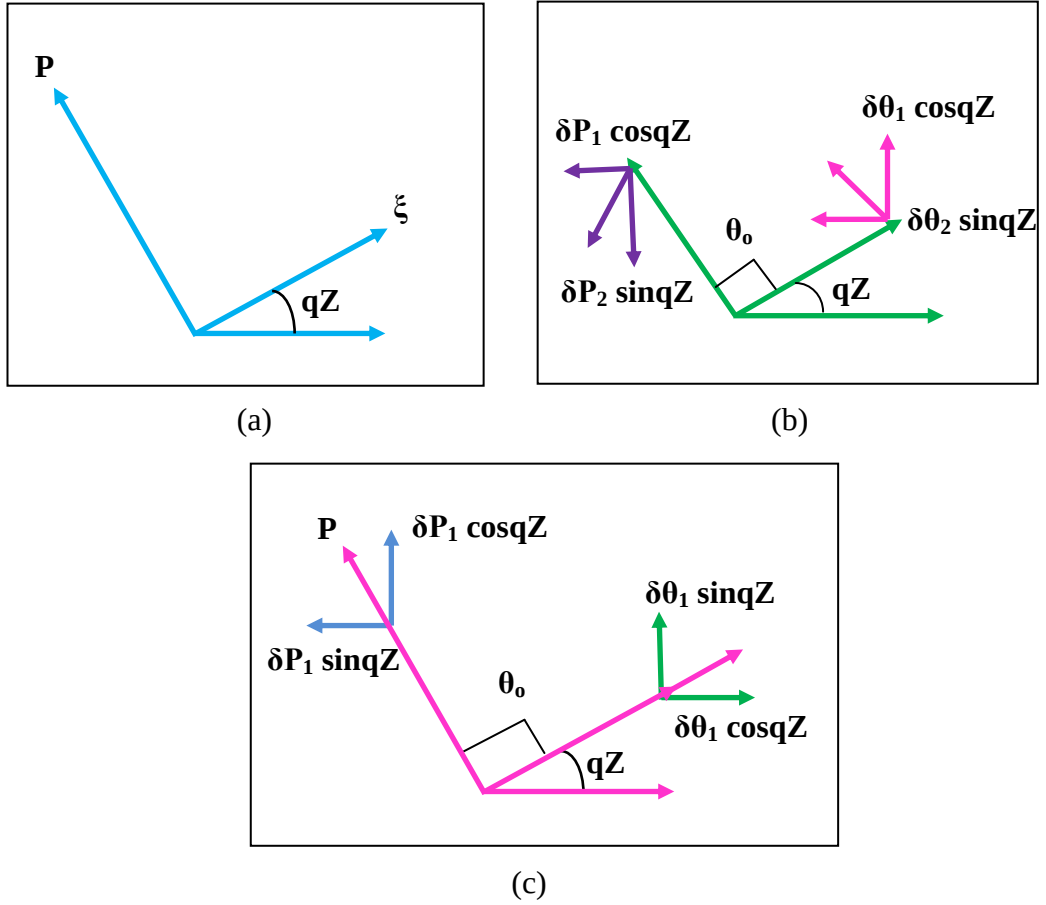


Figure 2.5 Representation of (a) the polarization and tilt order parameters (b) amplitude changes connected to soft mode (c) phase changes connected to goldstone mode [24].

The nature of polarization modes is rather puzzling and was first described by Carlsson et al. They described that these two modes appear due to the molecular rotation around long axis of the molecule. They also stated that the total dielectric permittivity is equal to the sum of permittivity due to the director fluctuations, polarization fluctuations and electronic contribution. They did not consider the non-collective excitations. This together with high absorption frequencies predicted for the polarization modes give impression that these are actually equivalent to the non-collective mechanism.

For each mode at a given temperature, contribution to the dielectric constant decreases with increasing frequency of the field from the low frequency value ($f \ll f_r$) to zero. This value is adopted when the value of applied field from the low frequency value of the applied electric field is so high ($f \gg f_r$) that the mode cannot follow the electric field. Here f_r is the characteristic relaxation frequency of that mode. The difference between the low and high frequency contributions of the mode to the total dielectric constant gives the dielectric strength of the mode. The dielectric strength is related to the average induced polarization as

$$\varepsilon_o \Delta \varepsilon(T) = \lim_{E \rightarrow 0} \frac{\langle P_i \rangle}{E} \quad (2.23)$$

where E is the magnitude of the static applied field. Here it has been assumed that fields acts as X-direction. On the other hand there exists a quadratic field effect, which originates in the dielectric anisotropy of molecules defined as

$$\delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \quad (2.24)$$

This describes the tendency of electric field to align the molecules with their axis of the largest dielectric susceptibility in the direction of field. Several relaxation mechanisms, each of which is connected to as characteristic relaxation frequency contributes to complex dielectric constant $\varepsilon^*(\omega, T)$ as given by eqn.2.7.

Distribution of relaxation times in chiral smectic phase

The frequency dependence of the complex dielectric permittivity in the SmC* phase ($\varepsilon_{\perp}^*$) when electric field is applied perpendicular to the molecules and parallel to the smectic layers can be presented as combination of two high frequency modes and two modes of lower frequency connected to the reorientation of the director is given by [16-26]

$$\varepsilon_{\perp}^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon_{GM}}{1+(i\omega\tau_{GM})^{1-\alpha_{GM}}} + \frac{\Delta\varepsilon_{SM}}{1+(i\omega\tau_{SM})^{1-\alpha_{SM}}} + \frac{\Delta\varepsilon_{PGM}}{1+(i\omega\tau_{PGM})^{1-\alpha_{PGM}}} + \frac{\Delta\varepsilon_{PSM}}{1+(i\omega\tau_{PSM})^{1-\alpha_{PSM}}} \quad (2.25)$$

Here the second term is related to GM and third term with the SM. Fourth and fifth term is connected with the molecular reorientation around their long and short molecular axes defined as the polarization goldstone mode and polarization soft mode.

In the SmA phase, $\theta_0 = P_0 = 0$, so that only amplitude changes are present. The system exhibits a double degenerated soft director mode and a double degenerated high frequency polarization mode. The complex dielectric permittivity in this case is written as

$$\varepsilon_{\perp}^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon_{SA}(T)}{1+(i\omega\tau_{SA})^{1-\alpha_{SA}}} + \frac{\Delta\varepsilon_{PA}(T)}{1+(i\omega\tau_{PA})^{1-\alpha_{PA}}} \quad (2.26)$$

$$\varepsilon_{\perp}^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon_{GM}(T)}{1+(i\omega\tau_{GM})^{1-\alpha_{GM}}} + \frac{\Delta\varepsilon_{SM}(T)}{1+(i\omega\tau_{SM})^{1-\alpha_{SM}}} \quad (2.27)$$

The SM contribution shows up practically in the vicinity of SmC*-SmA transition (T_{C^*A}). On approaching the transition, the elastic constant that constitutes the restoring force against the tilt fluctuations weakens or softens. These tilt fluctuations constitutes a soft mode which grows in strength as transition is approached. Not only has this softening of the elastic constant resulted in the increasing strength of the mode but also in the rapidly diminishing value of the relaxation frequency. Accordingly, we can say that soft mode is a mode that on approaching T_{C^*A} is characterized by

$$\varepsilon = \varepsilon_{\infty} \rightarrow \infty \text{ and } \omega \rightarrow 0 \quad (2.28)$$

The softening of this elastic constant means that the phase will lose its stability gradually until it becomes unstable and the molecules fluctuate collectively [fig.2.6 (b)].

When a weak electric field is applied in a direction perpendicular to the director in the SmC* phase, it can easily perturb the tilt fluctuation depending upon how close the system is to T_{C^*A} . The mechanism is usually observed in the kHz range with strong temperature dependence. In other words, the molecules collectively oscillate around the smectic cone. This mode is called GM [fig.2.6 (a)]. This process has a characteristic frequency which varies in the range of few kHz with weak temperature dependence. These modes are thermally activated. Both of them could be measured in the planer orientation [27].

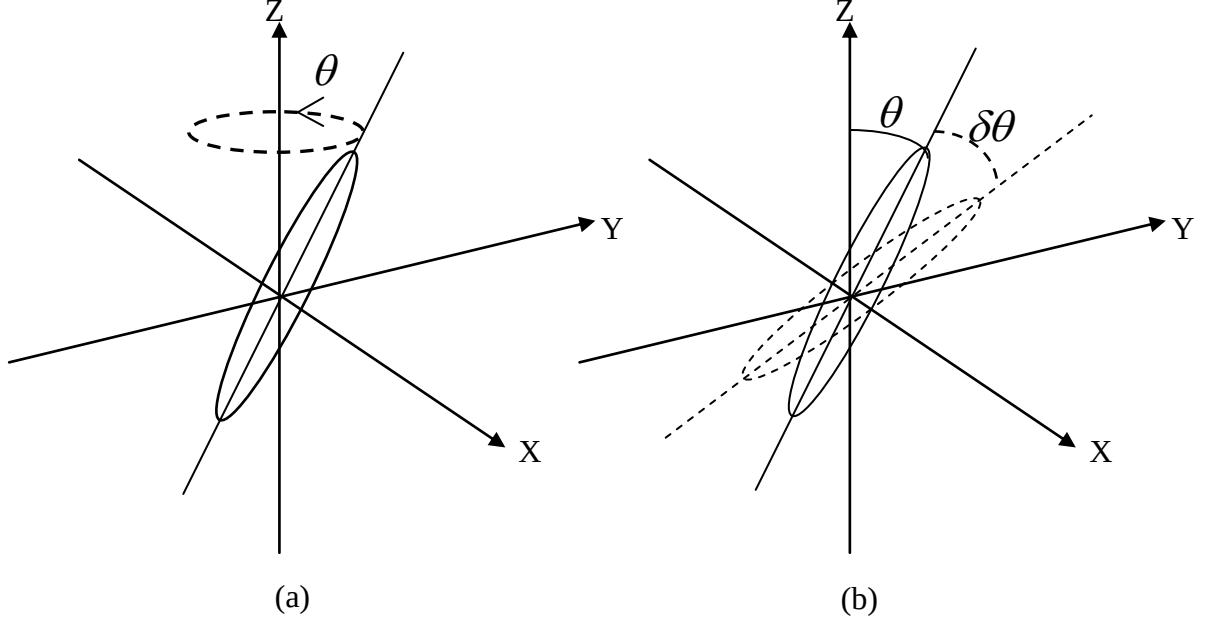


Figure 2.6 Geometry for the maximum (a) GM contribution & (b) SM contribution [6].

By splitting eqn.2.26 into real and imaginary parts, we obtain

$$\varepsilon'_{\perp}(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{0SM} - \varepsilon_{\infty}}{2} \left[1 - \frac{\sinh A}{\cosh A + \sin(\pi\alpha_{SM}/2)} \right] + \frac{\varepsilon_{0GM} - \varepsilon_{0SM}}{2} \left[1 - \frac{\sinh B}{\cosh B + \sin(\pi\alpha_{GM}/2)} \right] \quad (2.29)$$

$$\varepsilon''_{\perp}(\omega) = \frac{\varepsilon_{0SM} - \varepsilon_{\infty}}{2} \left[\frac{\cosh(\pi\alpha_{SM}/2)}{\cosh A + \sin(\pi\alpha_{SM}/2)} \right] + \frac{\varepsilon_{0GM} - \varepsilon_{0SM}}{2} \left[\frac{\cosh(\pi\alpha_{GM}/2)}{\cosh B + \sin(\pi\alpha_{GM}/2)} \right] \quad (2.30)$$

where

$$\left. \begin{aligned} A &= (1 - \alpha_{SM}) \ln(\omega\tau_{SM}) \\ B &= (1 - \alpha_{GM}) \ln(\omega\tau_{GM}) \end{aligned} \right\} \quad (2.31)$$

It was assumed that the molecular term (i.e. polarization modes and electronic mode) is included in ε_{∞} when our measurements are limited up to 1MHz range only.

The temperature and wave vector dependence of the order parameter excitation modes is obtained by using the generalized Landau model [28-29].

2.2.2 Non-collective polarization mechanism

The existence of collective dynamics is a consequence of ordering and hence collective fluctuations are unique to crystalline and liquid crystalline phases. In spite of long range nematic order, no collective mechanism of this phase can be excited by dielectric

spectroscopy due to the quadrupolar character of the nematic order. The same is valid for the materials possessing non-chiral smectic phases which show only non-collective relaxations.

The direction of molecular dipole moment depends upon the chemical structure of the compound and in general it may have component both parallel and perpendicular to the long axis of the molecules as shown in the fig.2.7 below [1].

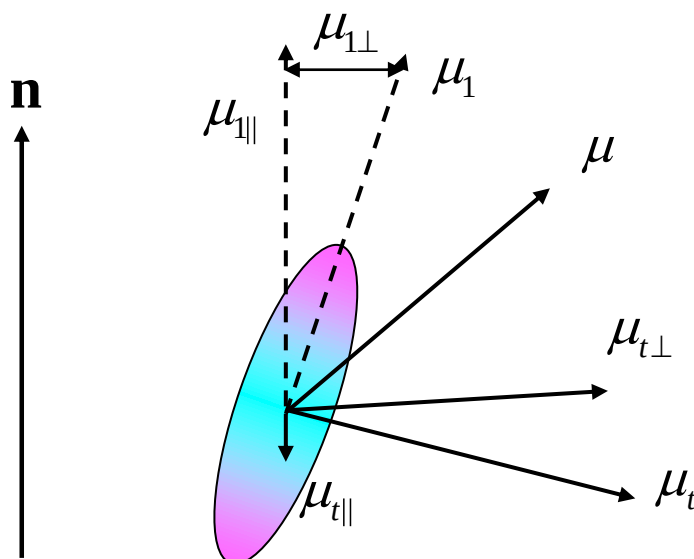


Figure 2.7 Component of dipole moment both parallel and perpendicular to the long axis of the molecules [6].

In the dielectric spectroscopy experiment, we apply a measuring field perpendicular to the plane of the cell i.e. perpendicular or parallel to the director depending upon whether the cell is homogeneously or homeotropically aligned. So only the dipole in the direction of the field will interact with it and give contribution to the dielectric permittivity. Since the re-orientational order is never perfect, both longitudinal and transverse dipole moment will in principle have a projection both along and perpendicular to the director but one component usually dominates heavily. In homeotropic alignment the field couples mainly to longitudinal dipole moment and field induced fluctuation bias is therefore equivalent to the re-orientation around the short molecular axis as shown in fig.2.8. If in the relaxed state, half of the molecules are oriented up and half are oriented down, an orientational polarization must effectively mean that the field flips the molecules. Such flips are much hindered and we expect the absorption frequency for this process to be substantially lower than in the isotropic phase. In planer, on the other hand, the similar

reasoning leads to the conclusion that the relative non-collective mechanism will be the re-orientation around the long axis.

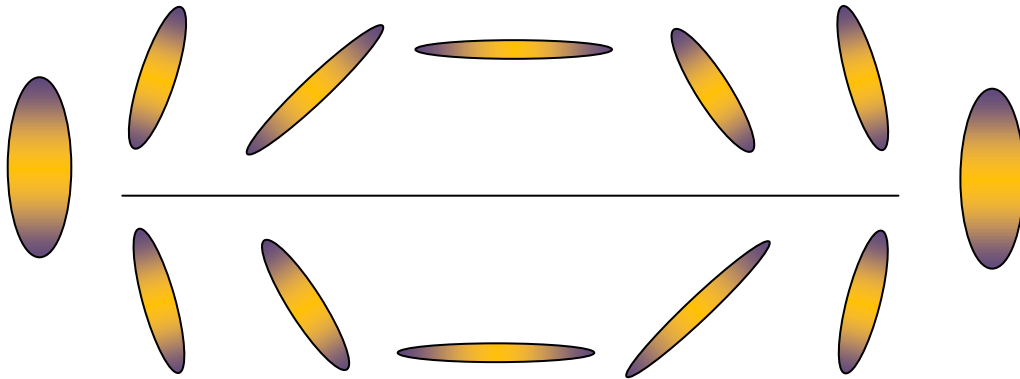


Figure 2.8 Re-orientation around the short molecular axis of the molecules [6].

2.3 THEORY OF ELECTRO-OPTICS

Electro-optics is the light modulation effect i.e. scattering and rotation of the plane of polarization. Liquid crystals are ideally suited for electro-optic devices. Ferroelectric liquid crystals possess bi-stability. These states can be readily switched with a time constant of few μs on application of external field. This switching time is related to the polarization and viscosity of the materials. The switching time can also be described in terms of dielectric strength and relaxation frequency of the goldstone mode [32]. The study of the switching of SmC^* phase is based on the following equation [33-38]

$$\eta \frac{d\varphi}{dt} = K \frac{\partial^2 \varphi}{\partial Z^2} - P_s E(t) \sin(\varphi) \quad (2.32)$$

where φ is the azimuthal and η is the rotational viscosity w. r. t. the rotations about smectic layer normal which defines z-direction. K is the mean elastic constant, P_s is the magnitude of spontaneous polarization of SmC^* phase and E is the amplitude of the applied electric field. It has been confirmed by experiments that normal vector and tilt angle (θ) between layer normal and director does not change on application of field parallel to the layers. However, the direction of the tilt changes resulting in the change of azimuthal angle (φ).

This molecular orientation can collectively takes place in the bulk and entire macroscopic polarization P_s is then effective driving force $P_s \times E = P_s E \sin\varphi$

$$\text{where } \phi(t) \cong 2 \tan^{-1} \left[\tan \left(\frac{\phi(0)}{2} \right) \exp \left(\frac{-t}{\tau} \right) \right] \quad (2.33)$$

For large t, we get

$$\phi(t) \cong 2 \tan^{-1} \left[\tan \left(\frac{\phi(0)}{2} \right) \exp \left(\frac{-t}{\tau} \right) \right] \quad (2.34)$$

which gives an exponential decay of $\phi(t)$ with τ given by

$$\tau = \frac{\eta}{P_s E} \quad (2.35)$$

This result was given by Clark and Lagerwall. The spontaneous polarization and response time could be measured with help of current reversal method.

2.4 TRANSMISSION STUDIES

In LCs, absorption of visible light is hardly there since it depends upon the various groups present. Since scattering is negligible in thin films, it implies that there will be maximum transmission of the incident light.

Optical transmittance

According to the theory based on Beer's law, optical transmittance is defined as

$$T = \frac{I_t}{I_o} = e^{-(\alpha+\beta)d} \quad (2.36)$$

The extinction coefficient γ can be defined as

$$\gamma = \alpha + \beta \quad (2.37)$$

where I_o , I_t are the incident and transmitted light intensity, d is sample thickness, α and β reflect scattering and absorption coefficients of the film respectively. α is a function of material properties.

Contrast ratio

The switching contrast ratio (CR) is usually defined as

$$CR = \frac{T_s}{T_o} \quad (2.38)$$

where T_o is the transmittance exhibited by the sample initially and T_s is the saturation value of the sample transmittance as the applied voltage increases shown in fig.2.9 [39].

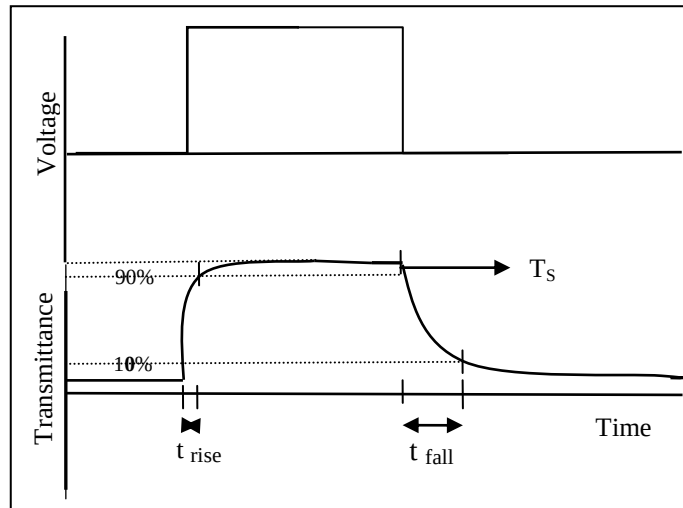


Figure 2.9 Output wave form obtained after applying peak to peak voltage in transmission studies [39].

Threshold voltage

Threshold voltage is defined as the minimum applied voltage at which transmittance reaches to 10% of the saturation transmittance. Below the threshold voltage, texture of the liquid crystal remains undistorted. As the voltage reaches above threshold voltage, distortion in director pattern is observed and effective birefringence of the cell is reduced.

Driving voltage

Driving voltage is defined as the minimum voltage required for the transmittance to reach 90% of the saturation transmittance.

Rise time and fall time

Rise time and fall time are defined respectively as the time for transmitted light intensity to go from 10% to 90% and 90% to 10% of the total change between the on and off states. The trends of both rise time and fall time are also visible in fig.2.9.

REFERENCES

- 1) Jan P.F. Lagerwall, Ph.D. Thesis, Chalmers University of Technology, Goteborg, Sweden (2000).
- 2) Vera V. Daniel, *Dielectric Relaxation*, Academic Press, NewYork (1967).
- 3) E Fattuzo, Ferroelectricity.
- 4) H. Frohlich, *Theory of Dielectrics: Dielectric Constant and Dielectric Loss*, Clarendon Press (1958).
- 5) Arthur R. von Hippel, *Dielectric Materials and Applications*, Technology Press of MIT and John Wiley, New York (1954).
- 6) Samriti Khosla, Ph.D. Thesis, Thapar Institute of Engineering and Technology, Patiala (2004).
- 7) S. Wrobel, G. Cohen, D. Davidov, W. haase, M. Marzec, M. Pfeiffer, *Ferroelectrics* **166**, 211 (1995).
- 8) R.B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. de Physique* **36**, L-69 (1975).
- 9) J. W. Goodby, *Mol. Cryst. Liq. Cryst.* **292**, 245 (1997).
- 10) H. Stegmeyer, A. Sprick, W. Kreiser and A. Weber, *Mol. Cryst. Liq. Cryst.* **1**, 263 (1995).
- 11) J.W. Goodby, *J. Mater. Chem.* **1**, 307 (1991).
- 12) N.A. Clark, M.A. Handschy, S.T. Lagerwall, *Mol. Cryst. Liq. Cryst.* **94**, 213 (1983).
- 13) M. Schadt, *Liquid Crystals* **5**, 57 (1989).
- 14) N.A. Clark and S.T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
- 15) L.A. Bersnav, L.M. Blinov, M.A. Osipov and S.A. Pikin, *Mol. Cryst. Liq. Cryst.*, **158**, 1 (1988).
- 16) S.L. Srivastava, *Proceedings of National academy of Science* (1993).
- 17) S. Wrobel, S. Hiller, M. Pfeiffer, M. Marzec and W. Haase, *Liq. Cryst.* **18**, 21 (1995).
- 18) A. M. Biradar, S. Wrobel and W. Haase, *Phys. Rev. E* **39**, 2693 (1989).
- 19) K.K. Raina and J.K. Ahuja, *Mol. Cryst. Liq. Cryst.* **325**, 157 (1998).
- 20) S. Hiller, a. M. Biradar, S. Wrobel and W. Haase, *Phys. Rev. E* **53**, 611 (1996).

- 21) K.K. Raina and J.K. Ahuja, Indian Journal of Pure and Applied Physics **38**, 504 (2000).
- 22) O. Hudak, J. Physique **44**, 157 (1983).
- 23) B. Urbanc and B. Zeks, Liq. Cryst. **4**, 1 (1989).
- 24) A. Levstik, T. Carlsson, C. Fillipic, I. Levstik and B. Zeks, Phys. Rev. A **35**, 3527 (1987).
- 25) C. Fillipic, T. Carlsson, A. Levstik, B. Zeks and R. Blinc, Phys. Rev. A **38**, 5833 (1988).
- 26) T. Carlsson, B. Zeks, C. Fillipic and A. Levstik, Phys. Rev. A **42**, 877 (1990).
- 27) Y. Kimura and R. Hayyakawa, Liq. Cryst. **14**, 427 (1993).
- 28) Y.P. Panarin, Huan Xu Seamus, T. Mac Lughadha and J.K. Vij, Jap. J. Appl. Phys. **33**, 2648 (1994).
- 29) J. Zubia, A. Ezcurra, M. R. DE La Fuente and M.A. Perfz Jubindo, Liq. Cryst. **10**, 849 (1991).
- 30) S. Markscheffel, A. Jakali and A. Saupe, Ferroelectrics **180**, 59 (1996).
- 31) A.M. Biradar, S. Hiller, S.A. Pikinand W. Haase, Liq. Cryst. **20**, 247 (1996).
- 32) Yu P Kalmykov and J.K. Vij, Liq. Cryst. **17**, 741 (1994).
- 33) Yu P Panarin and VM Vaksman, Mol. Mat. **1**, 147 (1992).
- 34) V. Panov, J.K. Vij and NM Shtykov, Liq. Cryst. **28**, 615 (2001).
- 35) J.K. Ahuja and K.K. Raina, Jap. J. Appl. Phys. **39**, 4076 (2000).
- 36) K.K. Raina and J.K. Ahuja, Mol. Cryst, Liq. Cryst. **338**, 125 (2001).
- 37) K.K.Raina and Samriti Khosla, Indian Journal of Pure and Applied Physics **42**, 49 (2004).
- 38) A.K. Gathania, B. Singh and K.K. Raina, Jap. J. Appl. Phys. **43**, 8168 (2004).
- 39) Leonid O. Dolgov and Oleg V. Yaroshchuk, Colloid. Polym. Sci. **282**, 1403 (2004).

CHAPTER 3

Sample Cell Preparation and Experimental Techniques

Overview

This Chapter includes the experimental techniques used for preparation and characterization of different nano materials doped ferroelectric liquid crystal composites to determine their dynamic responses. The various characteristics of ferroelectric liquid crystals and nano materials used in the experiments along with their phase sequences and molecular structure are given. A brief description of instruments used to study the thermo-optic, dielectric and electro-optic studies for the measurement of various physical properties of prepared composites is also provided.

3.1 MATERIALS USED

Various research groups are synthesizing and exploring new materials for their applications in electro-optical and display devices like light modulators, optical switches, high contrast and large area displays etc. Advancements in nanotechnology and astonishing characteristics of nano sized materials have given a new approach to further enhance the liquid crystal research. To achieve the desired performance of FLC devices, the selection of nano materials play an important role. In the present study, selection of the nano materials has been made to study the effect of nano materials with different sizes, shapes, physical and chemical properties on the dynamic responses of low and high polarization ferroelectric liquid crystals.

In the present work, we used in our experiments, the commercially available ferroelectric liquid crystal mixtures ZLI-3488 (FLC-I), ZLI 3654 (FLC-III) obtained from BDH, UK [1] and a synthesized ferroelectric liquid crystal material M10/6 (FLC-II) containing a lateral methyl group on the aromatic ring of the alkoxybenzoate unit [2]. The main components of the mixture FLCI are homologues of a new class of smectic cyclohexane derivatives with the structure given in fig 3.1 [3]. This compound has a good chemical stability, broad SmC* phase range, a negative dielectric anisotropy and a relatively small optical anisotropy. The molecular structure of FLCII is shown in fig. 3.2. The phase sequences obtained on cooling the FLC materials from their respective isotropic temperatures are given in Table 3.1. Transition temperatures in degree Celsius are provided in the figures, where Cr., SmC*, SmA, N*, and Iso. stand for crystalline, chiral smectic C phase, smectic A phase, chiral nematic or cholesteric phase and isotropic liquid

phase, respectively. The important physical parameters of ferroelectric liquid crystals used are also listed in Table 3.1. We studied the effect of silica nano particles (SiO_2) and multiwalled carbon nano tubes (MWCNTs) obtained from Sigma Aldrich [4] and synthesized nickel nanoparticles on the dynamic responses of FLCs. Their physical properties are given in Tables 3.2 and 3.3 respectively.

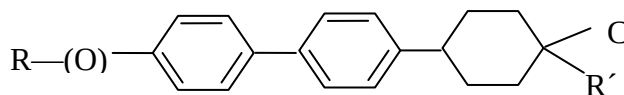


Figure 3.1 Molecular structure of the main components of FLCI.

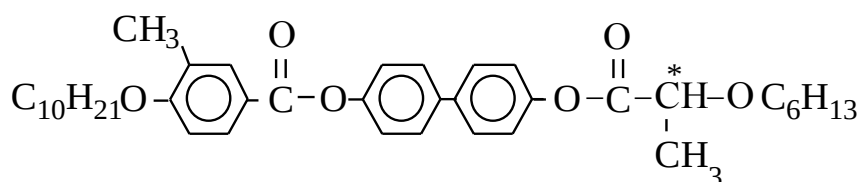


Figure 3.2 Molecular structure of FLCII.

3.2 FABRICATION OF LC CELLS

3.2.1 Liquid crystal cell alignment

Alignment of liquid crystal materials is the key component in LCD devices [5]. There is always a polymeric alignment on the inside surfaces of all the LCDs. The alignment layer provides both axis anisotropy (an axis) as well as polar anisotropy (a direction). Various methods have been proposed by various research groups to obtain uniform alignment. Mechanical rubbing of the surfaces with polyimide / PVA is most commonly used in the present technology. There are basic two types of alignments for aligning LC molecules [6-9]

1. Homeotropic alignment
2. Homogeneous alignment

Homeotropic alignment is obtained by the effect of geometrical structures. The optic axes of the constituent molecules of LC phase are oriented perpendicular to the glass substrates. When LC molecules are homotropically oriented, the polarized light is unaffected by the material, so light cannot pass through the analyzer and hence LC film appears black through the polarizing microscope under the crossed polarizers. Various

research groups have proposed different methods to obtain homeotropic alignment [10-12].

Table 3.1 Phase sequences and physical properties of the various FLCs used

FLCs	Phase sequence	Pitch (μm)	Tilt angle (deg.)	Ps (nC/cm ²)	τ_R (μs)
ZLI 3488 (FLCI)	-30°C 60°C 65°C 83°C $Cr \rightarrow SmC^* \rightarrow SmA^* \rightarrow N^* \rightarrow Iso$	12	25	9.7	$\sim 10^3$
M10/6 (FLCII)	5°C 98°C 105°C $Cr \rightarrow SmC^* \rightarrow N^* \rightarrow Iso$	1.5	42	240	~ 200
ZLI 3654 (FLCIII)	-30°C 62°C 66°C 86°C $Cr \rightarrow SmC^* \rightarrow SmA^* \rightarrow N^* \rightarrow Iso$	3	25	29	~ 44

Table 3.2 Physical properties of silica nano particles

Nano Materials	Form	Nano powder, Inorganic, Amorphous, Spherical, Porous
Silica(SiO_2)	Particle size (nm)	5-15
	Mol. Weight	60.08
	Surface Area (m ² /gm)	590-690
	M.P. ($^\circ\text{C}$)	>1600
	Density (g/ml at 25°C)	2.2-2.6

Table 3.3 Physical properties of multi walled carbon nano tubes

Nano Materials	Form	Multiwall carbon nanotubes
MWCNTs	Composition carbon	>90%
	Diameter (nm)	110-170
	Length (μm)	5-9
	M.P. ($^\circ\text{C}$)	3652-3697
	Density (g/mL at 25°C)	2.1

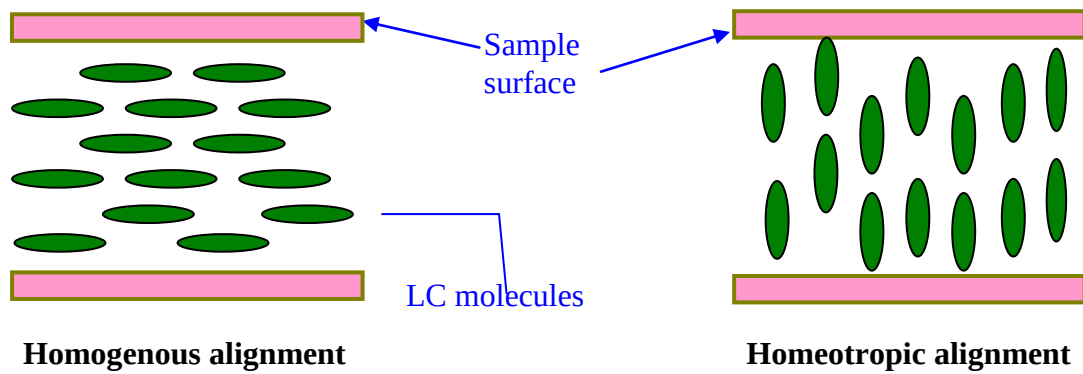


Figure 3.3: Homogeneous and homeotropic alignment [6-9].

Homogeneous alignment is obtained by unidirectional rubbing. Here the constituent molecules of LC phase are oriented parallel to glass substrates. This alignment is special in smectics and is known as “bookshelf alignment” since smectic layers are perpendicular to the substrate surfaces. This alignment is necessary to determine various FLC parameters like spontaneous polarization, tilt angle, helix pitch etc. Due to homogeneous alignment, LC films exhibit birefringence and hence coloured textures are obtained under cross polarizers of microscope. Different methods are used for homogeneous alignment of LC molecules like polymer rubbing, photo alignment, oblique evaporation of silicon monoxide etc.



Figure 3.4 Spin coating unit for polymer coating of glass substrates.

3.2.2 Polymer rubbing and empty cell construction

The empty sample cells were prepared by using conducting indium tin oxide (ITO) coated highly transparent glass substrates of about 200 ohm-m resistivity. They were first cleansed with soap solution, rinsed with acetone (99.9% pure), distilled water and then dried in vacuum chamber. Out of the two basic forms of alignment for liquid crystalline compounds or mixtures i.e. the homeotropic and homogenous [8-12], we used homogenous alignment method. The planer alignment was induced by spin coating (1400 rpm) polyimide (nylon) solution on the substrates using spin coating unit (fig.3.4).

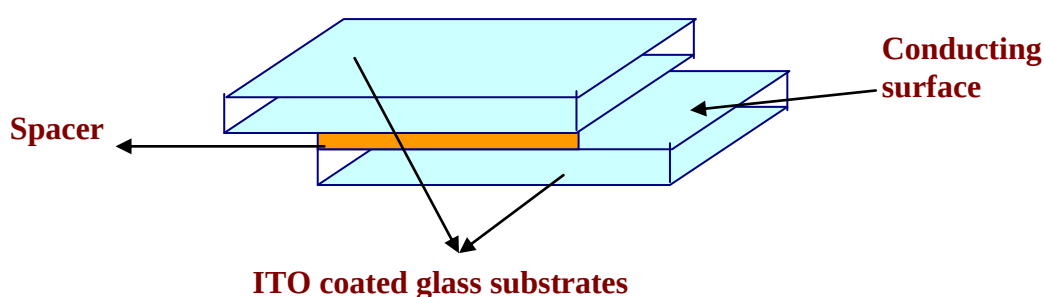


Figure 3.5 Assembled empty sample cell construction.



Figure 3.6 (a) Filled silica dispersed FLC sample cells with varying silica nanoparticles concentration

The solution of nylon was prepared in m-cresol and methanol. Both the glass substrates were rubbed unidirectionally with a nylon cloth encouraged the planer alignment [13-14]. In this method constituent molecules of the FLC phase are oriented parallel whereas smectic layers are oriented perpendicular to the supporting substrates. The conducting sides of these ITO coated glass substrates were joined together and separation between the substrates was maintained with the help of mylar spacer of 5 μ m thickness. The two sides of glass substrates were sealed using Norland optical adhesive epoxy glue (NOA-65) and other two sides were kept unsealed to fill the sample. Assembly of the empty sample cell is shown in fig.3.5.

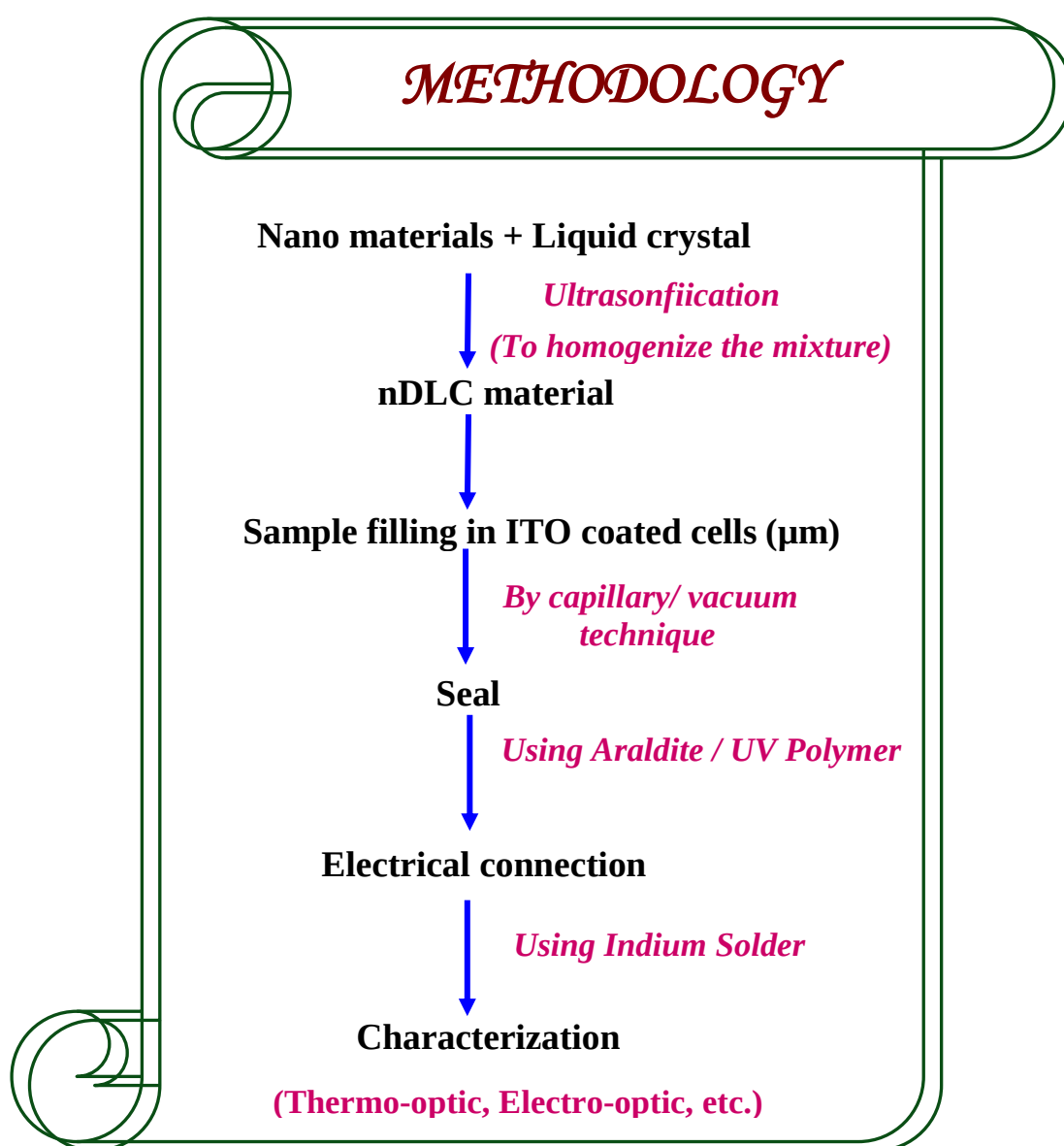


Figure 3.7 Flow chart for the preparation and characterization of nano dispersed ferroelectric liquid crystal composite cells.

3.3 PREPARATION OF NANO MATERIALS DISPERSED FERROELECTRIC LIQUID CRYSTAL COMPOSITES

The system of nano material-FLC composites were prepared by dispersing different wt/wt % of nano materials in the FLC matrix. The concentration 'x' of these particles was computed by $x = w_s / (w_s + w_{LC})$, where w_s and w_{LC} are weights of the nano materials and the FLCs in the nano materials-FLC composite systems. The dopant and the liquid crystal host were first mixed and then sonicated (36 kHz) for about an hour at the isotropic temperature to ensure uniform dispersion. The nano material-FLC composites were filled into the empty sample cells by capillary action and then sealed using Norland optical adhesive epoxy glue (NOA-65). The electric contact with the ITO coated substrate surfaces was made using indium solder. The cell assembly of various filled sample cells is shown in fig.3.6 (a, b). The characterization with respect to various dynamic responses of doped composites was carried out in homogenous (planar) cells. The various nano materials-FLC composites prepared are

- I. Silica nano particles dispersed ferroelectric liquid crystal composites
- II. MWCNTs dispersed ferroelectric liquid crystal composites
- III. Nickel nano particles dispersed ferroelectric liquid crystal composites

3.4 INSTRUMENTS USED AND EXPERIMENTAL TECHNIQUES

3.4.1 Phase identification and transition temperature studies

The phase transition temperature was determined by thermal polarizing microscopy and differential scanning calorimeter (DSC LINSEIS model L63). The morphological studies were carried out using polarizing microscope (Olympus model BX51P) fitted with digital camera (Olympus model DP12) interfaced to a computer system for recording and data acquisition. The sample was controlled to an accuracy of $\pm 0.1^\circ\text{C}$ using programmable temperature controller and hot stage (LINKAM model TP94 and THMS600).

Optical polarizing microscope

The optical studies observed in ferroelectric liquid crystal systems and nano dispersed ferroelectric liquid crystal composites were investigated using optical polarizing microscope at a magnification of 10X under crossed polarizers using long working distance objective lens. The textures were captured on a computer interfaced with polarizing microscope through Olympus camera (model DP12). The optical micro-

textures of LC materials were also investigated as a function of temperature, voltage and other physical parameters. The electric field was applied to the samples through SCIENTECH function generator (model ST4060). Fig. 3.8 shows the block diagram of experimental setup used for these studies.

Temperature programmer cum hot stage

We used Linkam temperature controller cum hot stage (model TP94 and THMS600) to perform thermal microscopic studies related to transition temperatures of various phases. The temperature controller has temperature range of -196°C to 600°C and is specifically designed for precise temperature control of the Linkam heating/freezing stages with accuracy $\pm 0.1^{\circ}\text{C}$ [15]. The stage sensor is digitally linearized to give accurate temperature readout. The controls and their functions have been carefully chosen for simple and easy operation. Heating or cooling rates can be changed almost instantly using the three rate keys. The various heat ranges are

From 0.1 to $0.9^{\circ}\text{C}/\text{min}$ at 0.1 degree intervals

From 1.0 to $9.0^{\circ}\text{C}/\text{min}$ at 1.0 degree intervals

From 10 to $90^{\circ}\text{C}/\text{min}$ at 10.0 degree intervals

A varying dc signal is used to control the stage and results in an even application of power, which avoids the bursts seen with conventional burst fire ac techniques. An optional remote control gives single key control of three programmable heating/cooling rates and the HEAT, COOL and HOLD functions. The three programmable heating/cooling rates are held in memory when power is switched OFF. The temperature and limit values can also be stored and recalled using the remote control facility.

Differential scanning calorimetry (DSC) measurements

Differential scanning calorimetry (DSC) is a thermal analysis technique that measures the heat flow to and from a specimen as a function of time and temperature. DSC is one of the most widely used analytical instrument because of the ease with which it can provide large amount of thermodynamic data. Properly used information on the phase transitions of a sample, such as transition temperature, enthalpy, heat capacity, specific heat, can all be calculated from a single data run. Enthalpy, a term often used in physical chemistry, is a measure of the energy of the system that includes the energy due to the volume that the system occupies. This experiment was an attempt to use DSC to examine

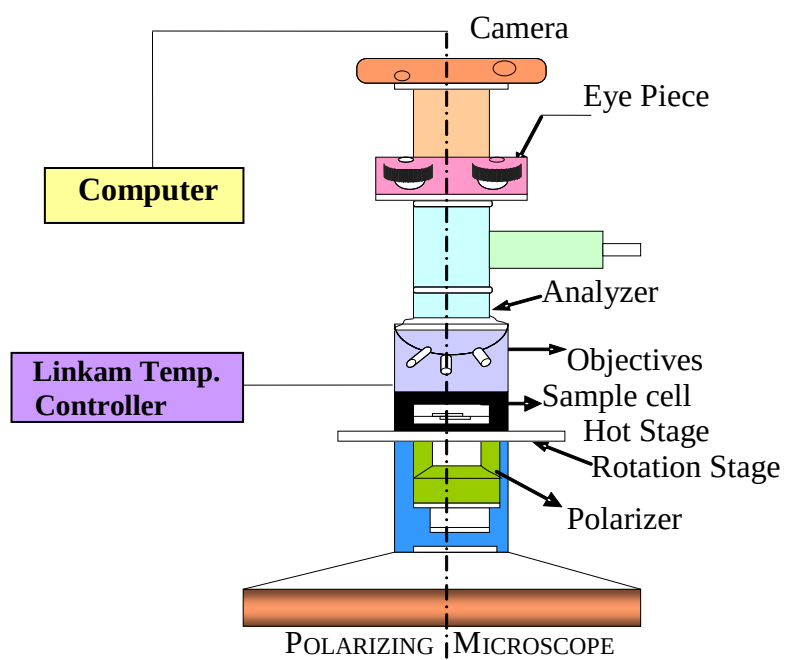


Figure 3.8 Block diagram of optical polarizing microscopy.

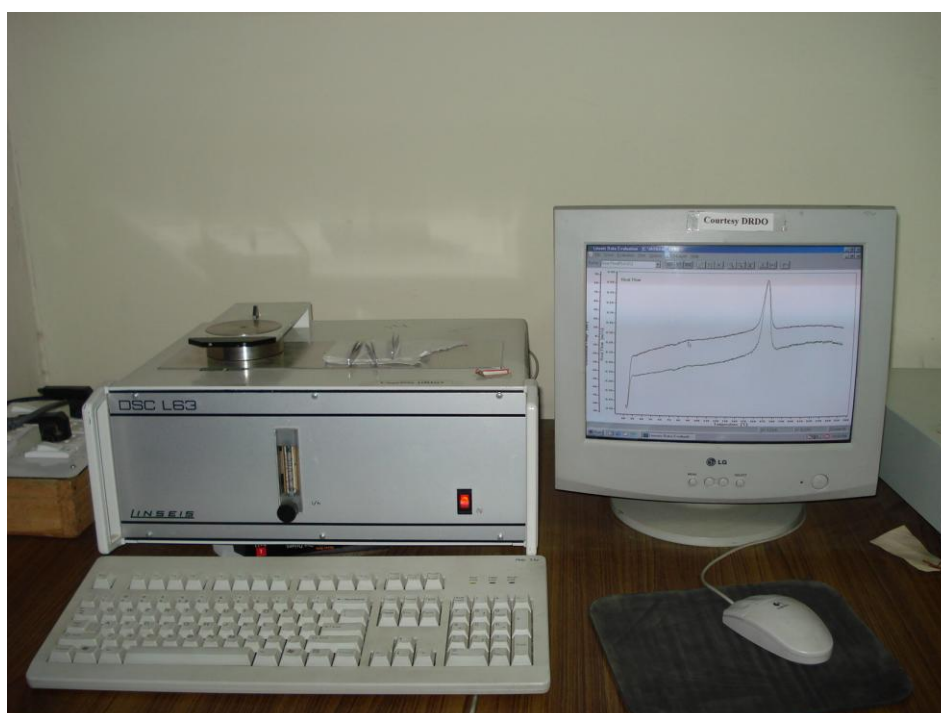


Figure 3.9 Differential scanning calorimeter.

the phase transitions and thermodynamic properties of the ferroelectric liquid crystals possessing a wide SmC* phase and nano materials dispersed ferroelectric liquid crystal composites containing different concentrations. The phase transition temperature of the

materials noted through thermal polarizing microscopy was fully supported by differential scanning calorimetry. The DSC (LINESEIS DSC L63) used in the experiment was controlled by a compatible computer running the LINESEIS DSC instrumental software [16]. The software collected data and provided graphical analysis tools to determine transition temperatures with measurement accuracy of ± 0 to 2 K. The DSC (LINESEIS model L63) used in the experiment is shown in the fig 3.9.

3.4.2 Dielectric studies

The dielectric studies were performed using Fluke RCL meter (model PM6306) in the frequency range 50 Hz-1MHz at different bias voltages and temperatures. The calibration of empty cells was done using benzene as standard solution. The experimental set up used for the dielectric measurements is shown in fig. 3.10.

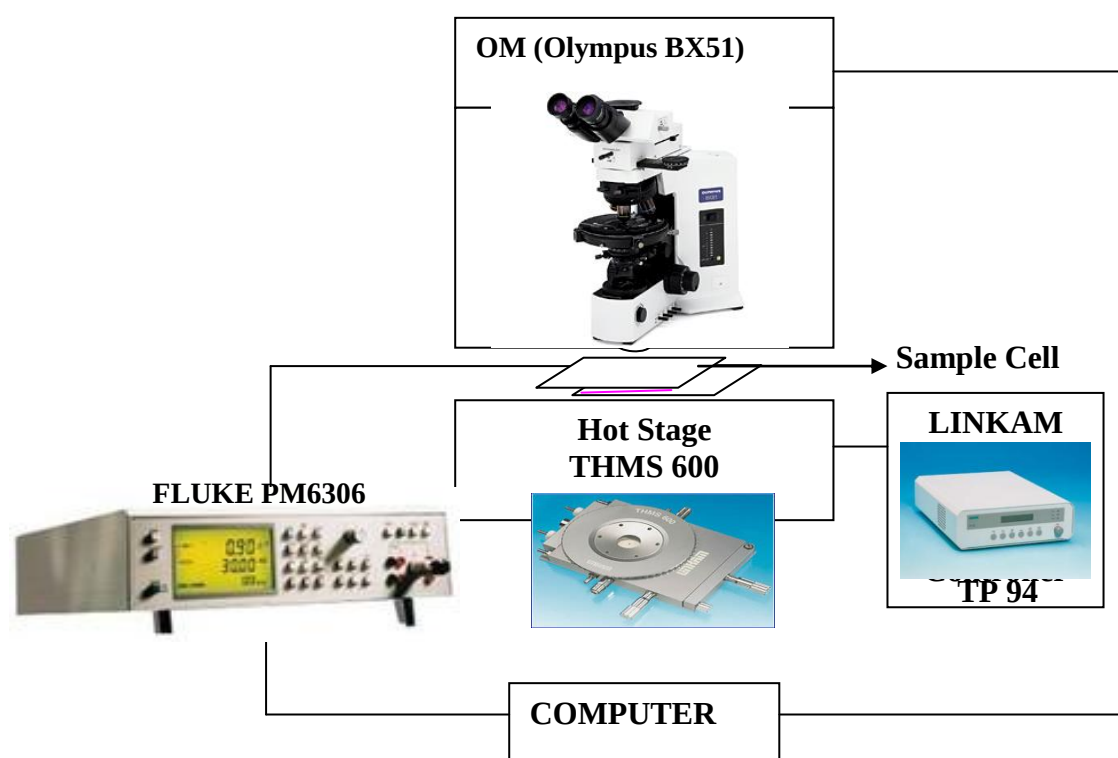


Figure 3.10 Block diagram of experimental set-up for dielectric measurements.

RCL meter (impedance analyzer)

The FLUKE model PM6306 RCL meter [17], with basic accuracy 0.1%, is fully automatic, high performance test instrument designed to measure a resistance, capacitance and inductance precisely. The one- measurement display sections provide

direct read out of the selected measurement parameters with the appropriate units. It also provides an average measurement mode to obtain measured data of high resolution and repeatability. The in-built frequency range can be set to the range from 50Hz-1MHz. The PM6306 can measure eleven impedance parameters i.e. absolute value of impedance $|Z|$, absolute value of admittance $|Y|$, phase angle (θ), resistance (R), reactance (X), conductance (G), susceptance (B), inductance (I), capacitance (C), dissipation factor (D) and quality factor (Q). Measurement range of L is 0.01mH to 1.0 kHz; C is 0.1 pF to 100 mF; D is 0.0001 to 19.999; Q is 0.1 to 1999.9.

Cell calibration

The measurement cell consists of a parallel plate capacitor connected with relatively short leads. The cell thickness is determined by the Mylar spacer or polyamide/ glass spacer between the glass plates. The vacuum capacitance for a capacitor having an area A and thickness t is given by [18]

$$C_o = 0.08854 \frac{A}{t} \times 10^{-12} \text{ Farad (where A and t are in cm)} \quad (3.1)$$

C_o represents the empty cell capacitance i.e. when the condenser is filled with air as a medium. The C_o has a contribution from the capacitance of the active area of the plates. The stray capacitance arises from the leads and non-homogeneities of the field lines at the edges of the active area. When extra capacitance (C_s) has been included as the edge capacitance (C_e) in two terminal measurements, the observed parallel capacitance (C_o) will be increased and observed dissipation factor (D_L) decreased. The correct values will be

$$C_L = C_o - C_e - C_g = C_o - C_s \quad (3.2)$$

$$D = \frac{C_L D_L}{C_p} \quad (3.3)$$

where C_L is the capacitance of the empty cell excluding the stray capacitance. When liquids are measuring in a two terminal measuring cell, the extra capacitance between electrodes and to ground unlike solids cannot be measured directly. The value of their combined capacitance ($C_e + C_g$) cannot be found by measuring the cell capacitance when filled to the same level by a liquid of known dielectric constant (C_x). From the capacitance of an empty cell and with a liquid of known dielectric constant (ϵ'_x), we get

$$C_s = C_e + C_g = \frac{\epsilon'_x C_o - C_x}{\epsilon'_x - 1} \quad (3.4)$$

From eqn.3.4 the value of C_s has been calculated. It is determined from measurements made on the standard liquids agrees within 1%. The dielectric permittivity (ϵ') of a LC material has been calculated using the simple relation [19]

$$\epsilon' = \frac{C - C_s}{C_o - C_s} = \frac{C - C_o}{C_L} + 1 \quad (3.5)$$

where C is the capacitance of the cell filled with a LC. The dielectric absorption has been calculated from loss (D) measurements [20] as given below

$$\epsilon'' = \epsilon' \times D = \frac{C \times D}{C_L} \quad (3.6)$$

Dielectric permittivity

The dielectric measurements were performed in the ferroelectric liquid crystals by using FLUKE RCL meter (model PM6306). For the perpendicular configuration, the orienting electric field was parallel to the smectic layers and perpendicular to the LC molecules. In this geometry, the capacitance and dissipation loss were measured directly from the RCL meter. The real (ϵ') and imaginary (ϵ'') parts of dielectric permittivity $\epsilon_\perp$ were calculated with the help of eqn. 3.5 and eqn. 3.6.

The qualitative evaluation of the dielectric measurements in the frequency range up to 1MHz is relatively straightforward. The measured dielectric absorption in the low frequency region has a contribution from the dipolar orientation and from the freely moving charges that has been correlated to get the actual value of permittivity of the LCs.

Dielectric strength and relaxation frequency

These parameters were calculated using Cole-Cole plots [21]. The semi-circle intersection with the ϵ' axis provides ϵ_0 and ϵ_∞ which represent dielectric permittivity at static and infinite frequencies respectively. Then dielectric strength can be calculated using the formula

$$\Delta\epsilon = \epsilon_0 - \epsilon_\infty \quad (3.7)$$

The Cole-Cole plot with a single relaxation time is shown in fig.3.11 (a). This plot can be considered in Cartesian co-ordinates but its treatment is mathematically more elegant in

the complex plane. A point on the semi-circle defines two vectors U and V. By virtue of the construction, $U - V = \epsilon_0 - \epsilon_\infty$ while $U = \epsilon'(\omega) - \epsilon_\infty + i \epsilon''(\omega)$ by definition.

If the Debye equations apply

$$V = U i \omega \tau \quad (3.8)$$

which signifies that the two vectors are at right angles to each other, since multiplication by 'i' signifies rotation by $\pi/2$ in the complex plane.

Cole-Cole generalized the representation of a Debye dielectric by a circular arc plot in the complex plane so that it applies to a certain type of distributions of relaxation times [fig.3.11 (b)] and it is defined as

$$\frac{V}{U} = (\omega \tau)^{1-\alpha} \quad (3.9)$$

$$\text{where } V = \left[\left\{ \epsilon_0 - \epsilon'(\omega) \right\}^2 + \left\{ \epsilon''(\omega) \right\}^2 \right]^{1/2} \quad (3.10)$$

$$\text{and } U = \left[\left\{ \epsilon'(\omega) - \epsilon_\infty \right\}^2 + \left\{ \epsilon''(\omega) \right\}^2 \right]^{1/2} \quad (3.11)$$

$\epsilon'(\omega)$ and $\epsilon''(\omega)$ have been calculated using eqn. and eqn. τ and α are the relaxation time and distribution parameter of the corresponding relation time ($= 1/2 \pi f_r$). Here f_r is the relaxation frequency of the relaxation mode.

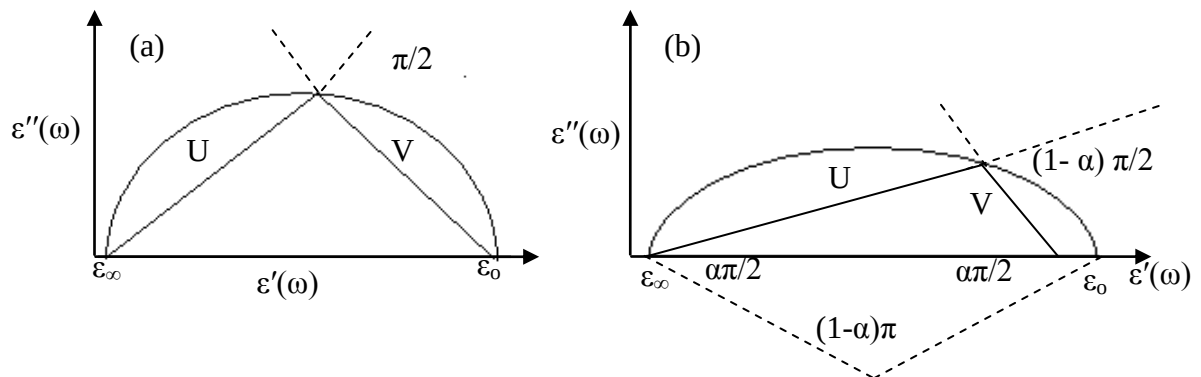


Figure 3.11 (a) Arc plot for a Debye dielectric and (b) arc plot for a dielectric with a Cole-Cole distribution characterized by parameter α [14].

The plot of $\log_{10} (V/U)$ vs $\log_{10} f$ gives a straight line. The intercept of the abscissa corresponds to f_r and the slope gives the distribution parameter α . The data points may deviate from the straight line because at low frequencies value of (V/U) is very small as V is small and at high frequencies (V/U) is large as U is small. This makes the value of $\log_{10} (V/U)$ very sensitive to the choice of $C(0)$ and $C(\infty)$ [22].

3.4.3 Polarization switching studies

Resistance method/ current reversal method

Resistance method or Current reversal method is one of the accurate methods used for the measurement of various electro-optic parameters [14, 18]. It measures the current induced by the application of triangular and square wave pulses. While the triangular wave method is widespread due to its simplicity, the square wave method provides more rigorous measurements. The triangular wave method gives a direct measurement of spontaneous polarization whereas square wave method measures response time as well as polarization of the sample.

Fig 3.12 shows the experimental set-up used for these studies. Here, the triangular or square wave pulses were applied across the sample cells through a function generator (SCIENTECH ST4060). The output was taken across a standard resistor and obtained on the digital oscilloscope (Tektronix TDS210) interfaced with the computer for further data acquisition. Data analysis was done using *wavestar* software.

In order to study the molecular reorientation process associated with the helix dynamics, the symmetric, -10V - 0V - +10V (20V peak to peak)) triangular and square wave voltage was applied to the FLC composites. It reorients the dipoles between two stable polarization states (Up and Down). As the field is switched on, molecular alignment in the form of voltage drop is detected on the storage oscilloscope.

In the SmC* phase, for a certain applied field, the output current response across the standard resistor R consist of three components

- (i) Ionic contribution term I_R
- (ii) Capacitor term I_C due to charge accumulation in the capacitor
- (iii) Polarization current term I_P due to charge induced by dipole realignment in the form of polarization hump

Thus, the instantaneous value of output current across the resistor can be written as

$$I = I_R + I_C + I_P = \frac{V_{IN}}{R} + C \frac{dV_{IN}}{dt} + A_s \frac{dP}{dt} \quad (3.12)$$

where C is the capacitance and A_s is the area of the cell respectively.

In this method, too low frequencies are applied which are necessary for switching the polarization in relatively viscous substances. The frequency of the external voltage must be lower than the inverse of relaxation time for the director depending on sample thickness, anchoring energy, defects etc. Here voltage is chosen high enough to unwind

completely the helical structure of FLC. Thus the measured value of P_s does not include the flexoelectric contribution which just results from a non-uniform structure.

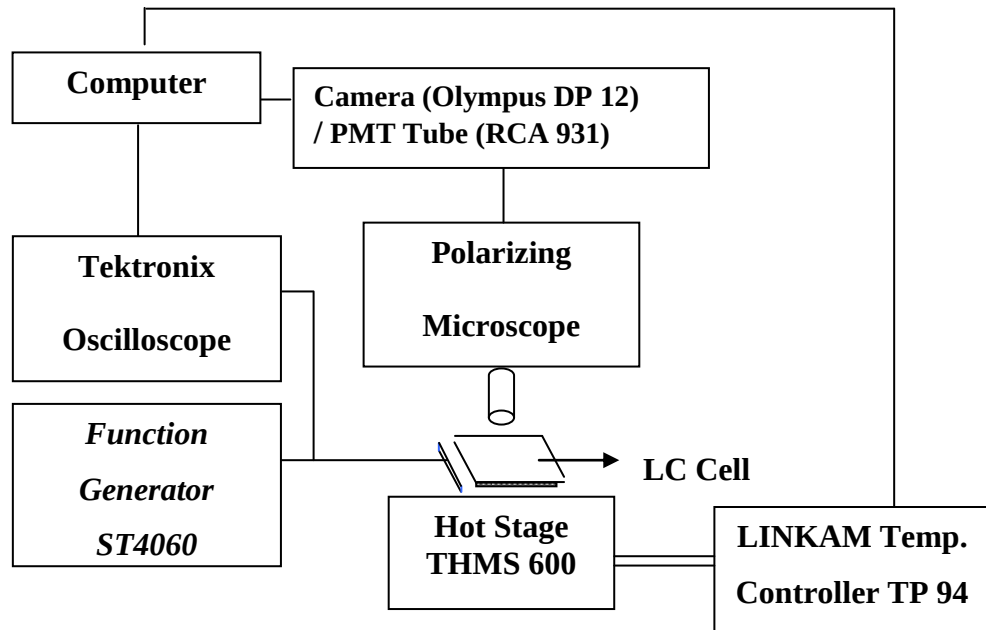


Figure 3.12 Block diagram of experimental set-up used for electro-optic studies.

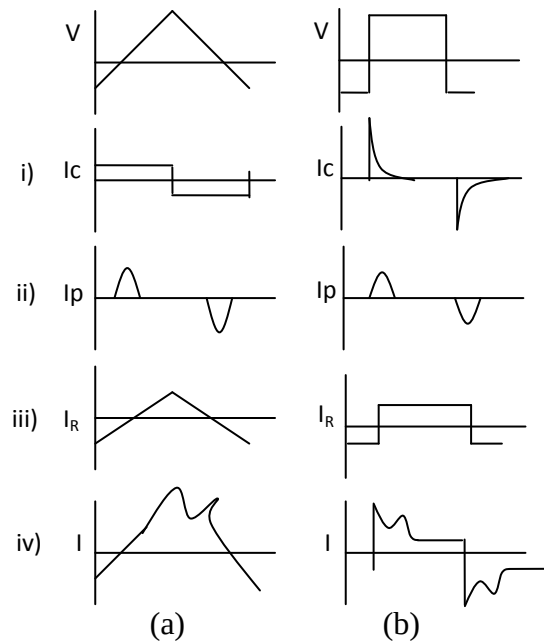


Figure 3.13 (a) Triangular wave output and (b) square wave output [14].

These electro-optic studies were also confirmed by using automatic *gain phase analyzer* (Solartron 1260) at National Physical Laboratory, New Delhi, India.

Spontaneous polarization

The spontaneous polarization P_s is the macroscopic polarization, which the sample attains due to the coupling of polarization P with the electric field E within the layer normal. The sample gets poles and attains a macroscopic polarization. At this stage, the helix of the FLC sample confined in the cell of a particular thickness unwinds; the macroscopic polarization becomes non zero and the sample gets spontaneously polarized.

Polarization measurements were taken by applying a symmetric triangular wave of 50Hz frequency and sufficient voltage for complete unwinding of the helix. The effects of resistive and capacitive terms have been subtracted by drawing a base line as shown in fig.3.13 (a). The polarization current I_p is due to charge induced by the dipole realignment in the form of polarization. The polarization hump is directly associated with dipole reorientation corresponding to the switching between two stable states. Every reorienting dipole imparts a charge impulse and contributes to the polarizing reversal peak. Thus, the peak incorporates total contribution of reorientation dipoles while switching between uniform states. However, by using an asymmetric wave, the peaks corresponding to the polarization hump directly gives the measure of polarization in the sample on application of field [23].

$$\begin{aligned} 2 A_s P_s &= \text{area under the curve (current} \times \text{time)} \\ &= A (I \times t) \end{aligned}$$

$$\text{Hence } P_s = \frac{A(I \times t)}{2A_s} \quad (3.13)$$

where A_s is the area of the sample. Thus by calculating the area of the curve by knowing current and time representation along the y-axis and x-axis respectively, P_s can be calculated. Temperature dependence of polarization follows the following power law

$$P_s = A_s (T_C - T)^\beta \quad (3.14)$$

Here β is the critical exponent and its value is 0.5 as predicted by the mean field theory.

Response time

Response time (τ_R) is defined as the delayed switching between two stable states. It has been measured using a symmetric square wave, which gives a simultaneous measurement of P_s and τ_R . From the behaviour of polarization reversal current [fig.3.13 (b)], it is clear that the polarization peak appears far away from the time scale from the square pulse edge of the applied wave. The delay in the time corresponds to the response time of

switching between the stable states of polarization and represents the time in which the average number of molecules reorients after applying the pulse. This representation of the response time from the current signal coincides with the electro-optic switching (i.e. the time required to change the optical transmission from 10% to 90% as shown in fig. 2.9, chapter 2).

Rotational Viscosity

Rotational viscosity corresponds to the molecular rotation of the director about its layer normal. In a FLC system, we have

$$\tau = \frac{\eta_R}{P_S \cdot E} \quad (3.15)$$

$$\text{Hence } \eta_R = \tau P_S E \quad (3.16)$$

where η_R is the effective rotational bulk viscosity and E is applied the electric field. The temperature dependence of the rotational viscosity follows Arrhenius law given by

$$\eta_R = A e^{\frac{-E_a}{KT}} \quad (3.17)$$

where E_a is the activation energy and K is the Boltzmann constant.

Activation energy (E_a)

By fitting the temperature vs rotational viscosity curve we can calculate the activation energy of the sample. It can also be calculated from the plot of relaxation frequency of GM as a function of temperature which shows an Arrhenius type of behaviour given by

$$f_r = f_o \exp(-E_a / KT) \quad (3.18)$$

where f_r is the relaxation frequency and f_o is a constant. The slope of the relaxation frequency curve corresponds to activation energy.

3.4.4 Transmission studies

The Transmission studies were carried out when an electric field was applied to the sample using a function generator (model ST4060) [24]. The output responses were recorded and detected on digital storage oscilloscope (Tektronix model TDS 2024) using a photo-multiplier tube (model RCA 931A) with a power supply of 1000 Volts. Block diagram for the experimental arrangement is shown in fig. 3.12. Various parameters like optical transmittance, contrast ratio, threshold voltage and driving voltage etc. were measured using different relations given in section 2.4 of chapter 2.

3.4.5 Tilt angle measurements

The measurement of the tilt angle of the FLCs can be carried out by the application of square waveform voltage [25].

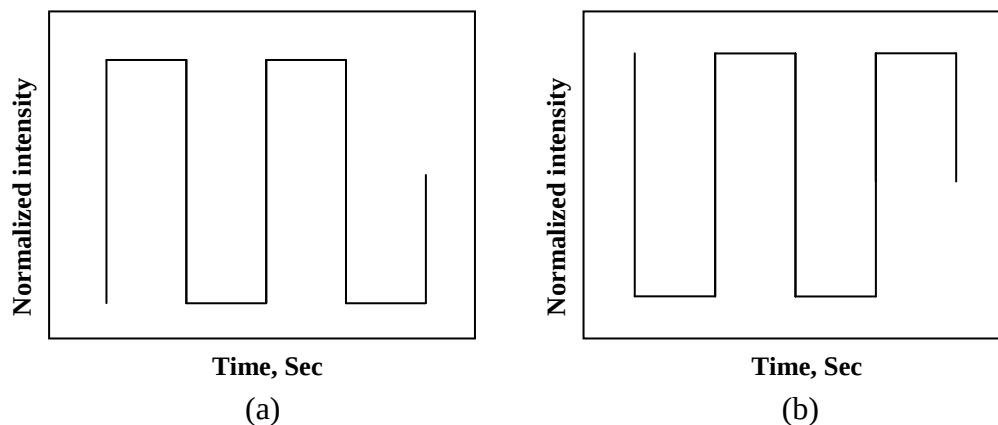


Figure 3.13 Measurement of the tilt angle θ ; typical form of electro-optical response at two extreme positions of the cone: (a) angle θ ; (b) angle $-\theta$ [25].

In this case, the switching can be easily detected by the above-described setup for transmission studies. In order to do it, one should turn the rotation table in such angular position that one of the extreme positions of the cone (say θ) coincides with the transmission axis of the analyzer. The transmission of the light becomes equal to zero. By applying the electric field, the transmitted intensity increases [fig.3.13 (a)]. Then, if the cell is rotated to the opposite position ($-\theta$) coinciding with a polarizer, the electro-optical response change its polarity [see fig.3.13 (b)]. This means that the cell is turned at angle of 2θ . The value of the tilt angle θ can be easily derived from it.

3.4.6 UV-VIS Spectrophotometer for absorbance studies

Ultraviolet-visible spectrophotometry (UV-VIS) refers to absorption spectroscopy in the ultraviolet-visible spectral region. It uses light in the visible and adjacent (near-UV and near-infrared) ranges. The absorption in the visible range directly affects the perceived color of the materials involved. Molecules undergo electronic transitions in this region of the electromagnetic spectrum. Absorption measures transitions from the ground state to the excited state. The UV-VIS absorbance of undoped and doped samples was investigated at room temperature using UV-VIS spectrophotometer (Analytik Jena's Specord 205) in the wavelength range of 200-800nm. The output responses were obtained on the computer interfaced to the spectrophotometer.

REFERENCES

- 1) BDH, UK.
- 2) M. Kaspar, V. Hamplova, S.A. Pakhomov, I. Stibor, H. Sverenyak, A. Bubnov, M. Glogarova and P. Vanek, *Liq. Cryst.* **22**, 557 (1997).
- 3) C. Eschar, T. Geelhaar, E. Bohm, *Liq. Cryst.* **3**, 469 (1988).
- 4) Sigma Aldrich, Germany.
- 5) B. Bahadur, *Liquid Crystals: Applications and Uses*, World Scientific, Singapore, Vol. **3** (1992).
- 6) S. Chandrasekhar, *Liquid Crystals*, 2nd Edn, Cambridge University Press (1992).
- 7) P. G. De Gennes, *Physics of Liquid Crystals*, Oxford University Press (1975).
- 8) I.C. Khoo, *Physics of Liquid Crystalline Materials* (Amsterdam: Golden and Breach) (1991).
- 9) P. J. Collings, *Liquid Crystals: Nature's Delicate Phase of Matter*, Princeton University Press (1990).
- 10) K. Hiroshima, *Jpn. J. Appl. Phys.* **21**, L761 (1982).
- 11) W. Urbach, M. Boix and E. Guyon, *Appl. Phys. Lett.* **25**, 479 (1974).
- 12) S.S. Bawa, A.M. Biradar and S. Chandra, *Jpn. J. Appl. Phys.* **25**, L446 (1986).
- 13) J.K. Ahuja and K.K. Raina, *Jpn. J. Appl. Phys.* **39**, 4076 (2000).
- 14) J.K. Ahuja, Ph.D. Thesis, Thapar Institute of Engineering and Technology (2000).
- 15) Manual of Linkam Temperature Controller (TP94) and Hot Stage (THMS600).
- 16) Manual of Differential Scanning Calorimeter (Lineeis DSC L63).
- 17) Manual of RCL meter (Fluke PM 6306).
- 18) Samriti Khosla, Ph.D. Thesis, Thapar Institute of Engineering and Technology (2004).
- 19) M.A. Handschy, Ph.D. Thesis, University of Colorado, USA (1984).
- 20) S.S. Bawa, A.M. Biradar and S. Chandra, *Jpn. J. Appl. Phys.* **26**, 189 (1987).
- 21) R.T. Morrison and R.N. Boyd, *Organic Chemistry VIth edition*, prentice Hall of India, New Delhi (1999).
- 22) A. Jakali, L. Bata and E. Eber, *Ferroelectrics* **85**, 187 (1988).
- 23) K.K. Raina and J. K. Ahuja, *Mol. Cryst. Liq. Cryst.* **338**, 125 (2001).
- 24) Pankaj Kumar and K. K. Raina, *Curr. Appl. Phys.* **7**, 636 (2007).
- 25) Fedor V. Podgornov, Ph.D. Thesis, Darmstadt University (2004).

CHAPTER 4

Silica Nanoparticles

Dispersed

Ferroelectric Liquid

Crystal Composites

Overview

We present experimental results based on the dispersion of silica nano particles in a room temperature ferroelectric liquid crystal system. The thermo-optic, dielectric and electro-optical responses of silica-FLC composite films have been studied in detail. The dielectric parameters of doped FLC cells exhibit an anomalous dependence on the silica concentration. Various relaxation modes have been observed with relaxation frequencies in the range of 50 Hz to 200 kHz. The effects of silica concentration on the spontaneous polarization, tilt angle, switching time and rotational viscosity were also examined with temperature and voltage. In addition, the concentration of silica is changed to improve the film performance and determine the best electro-optic responses in terms of important parameters, such as threshold voltage, driving voltage, optical transmission and contrast ratio as a function of applied voltage, temperature and silica concentration. Our result indicates that high silica concentration FLC composite shows better optical properties and higher contrast ratio. These anomalous results are attributed to the homeotropic orientation of liquid crystal molecules in the presence of silica nano particles without applying any external field.

4.1 INTRODUCTION

In the recent past, several research groups have studied the dispersion of nano particles in the LC matrix to prepare novel functional materials for enhancing their electro-optic properties for device performances [1-6] and better understanding the science of the dispersed soft condensed matter. The astonishing advantage of nano materials dispersion into liquid crystal matrix is the tunability of electro-optical properties of nano materials with the structural and functional flexibilities of LCs. Reznikov et al. reported that the physical properties of these composites can be controlled by dispersing low concentration of the nanoparticles in the LC matrix [5]. He showed that they did not change the elastic properties of host LC, but rather improved the electro-optic response function of the composite system.

Silica nano particles dispersion in the nematic liquid crystals have been studied by various research groups in detail [7-21]. The unique migrating behaviour of silica particles in LC matrix could generate some point defects in liquid crystals which scatter light. However, application of an external electric field causes reorientation of LC

molecules and transformation of defects that result into a weakly scattering state. Two complex behaviours have been reported [9-11] after field removal; either the system relaxes back to a scattering state i.e. the orientation induced by electric field remains stable after removing the field or memory effect. The memory effect characteristics depend upon chemical composition of nano particles and liquid crystals. This memory is assumed to be due to formation of hydrogen bonds that enhance anchoring energy [22].

Dispersion of silica nano particles into liquid crystals lead to ordering and structural properties of liquid crystals. These particles give rise to disclinations in the director field due to incompatibility between boundary conditions on particle surface that result into effective anisotropic inter-particle interactions [23-24] which depend on interaction energy between LC molecules, nano particle surfaces and elastic constants of liquid crystal. Electrostatic analogy describes formation of chain like structures due to long range attractive forces induced by orientational fluctuations between particles in anisotropic meso-phases. For a given inter particle distance 'd' in smectics, these attractive forces are $\propto 1/d^2$ and are longer in range than the van der Waals forces.

Silica particles in smectic liquid crystals with layered structure form a quite different, interesting and complicated system than nematic systems. The impurity particles can much easily move parallel to the smectic layers as compared to perpendicular because viscosity is larger in perpendicular direction to the smectic layers [23, 24]. Particle movements in smectics lead to high distortion energy but bending and twisting are constrained. Also dynamics of particles strongly depends upon geometry of the cell.

Some research groups have also studied the dielectric spectroscopy in the chiral smectic C LCs in detail [22, 25-27]. The behavior of various relaxation modes like goldstone (GM) and soft (SM) has been reported in them due to the collective molecular motions. Cordoyiannis et al. revealed novel properties in hydrophilic silica dispersed FLCs which are important to understand quenched disorder and confinement in FLCs [28].

In the current research work, we have reported the effect of small concentrations of silica nano particles on the dielectric spectroscopy and electro-optic dynamic responses of a FLC mixture.

4.3 EXPERIMENTAL DETAILS

A system of FLCI-silica composite materials was prepared by dispersing 0.01, 0.02, 0.05 and 0.1 wt/wt % of SiO₂ particles in the ferroelectric liquid crystal I (FLCI) matrix. The

concentration 'x' of these particles was computed by $x = w_s / (w_s + w_{LC})$, where w_s and w_{LC} are weights of the silica nano particles and the FLCI mixture in the silica- FLCI composite systems.

The morphological studies were carried out using polarizing microscope (Olympus model BX51P) fitted with Olympus camera (model DP12) interfaced to a computer system for recording and data acquisition. The sample was controlled to an accuracy of 0.1°C using programmable temperature controller and hot stage (LINKAM Model TP94 and THMS600). The dielectric studies were carried out using Fluke RCL meter (model PM6306) in the frequency range 50 Hz-1MHz at different bias voltages and temperatures. The calibration was done using benzene as standard solution.

The electro-optical measurements were carried out using the experimental setup reported in chapter 3 (fig. 3.12). Each sample cell was set between two crossed polarizers and peak to peak voltage of 0-30V (at frequency $f = 50\text{Hz}$) was applied to calculate their various electro-optic parameters such as spontaneous polarization, response time etc. The transmission studies were performed using photo-multiplier tube (model RCA 931) and digital storage oscilloscope (model Tektronix TDS 2024) to calculate electro-optic contrast, threshold and driving voltages.

4.4 RESULTS AND DISCUSSION

4.4.1 Isotropic temperature

Doping of silica nano particles has influenced the isotropic temperature of the LC. A slight positive shift of about +1°C in the transition temperature of various phases have been noticed after SiO₂ doping. The corresponding temperature values are given in Table 4.1. This temperature shift suggests strong interactions between FLC molecules and silica nano particles on the molecular level which results into an anisotropic alignment of FLC molecules induced by SiO₂ nano spheres and hence the isotropic temperature increases [15]. The increase in isotropic temperature of SiO₂ doped samples is also supported by their morphological studies discussed in section 4.4.2.

4.4.2. Texture morphology

The optical textures were evaluated on cooling the various samples from their isotropic temperatures under the crossed polarizers. Fig. 4.1 shows sequence of events in the growth of optical textures in 0.1 wt/wt % SiO₂ doped FLCI composite. At 86°C, the

material exhibits an isotropic phase under crossed polarizers, whereas at 84°C we observed the nucleation of batonets which coalesced into elongated chiral nematic domains and got aligned into chiral smectic C phase texture as shown in fig. 4.2.

Table 4.1: Investigated isotropic temperature of silica doped samples

Samples	$T_{\text{SmC}^*-\text{SmA}}$ (°C)	$T_{\text{SmA}-\text{N}^*}$ (°C)	$T_{\text{N}^*-\text{I}}$ (°C)
Undoped FLCI	60.0	65.0	83.0
FLCI + 0.01 wt % SiO_2	60.3	65.1	83.0
FLCI + 0.02 wt % SiO_2	60.3	65.4	83.2
FLCI + 0.05 wt % SiO_2	60.4	65.6	83.4
FLCI + 0.1 wt % SiO_2	60.7	65.9	84.0

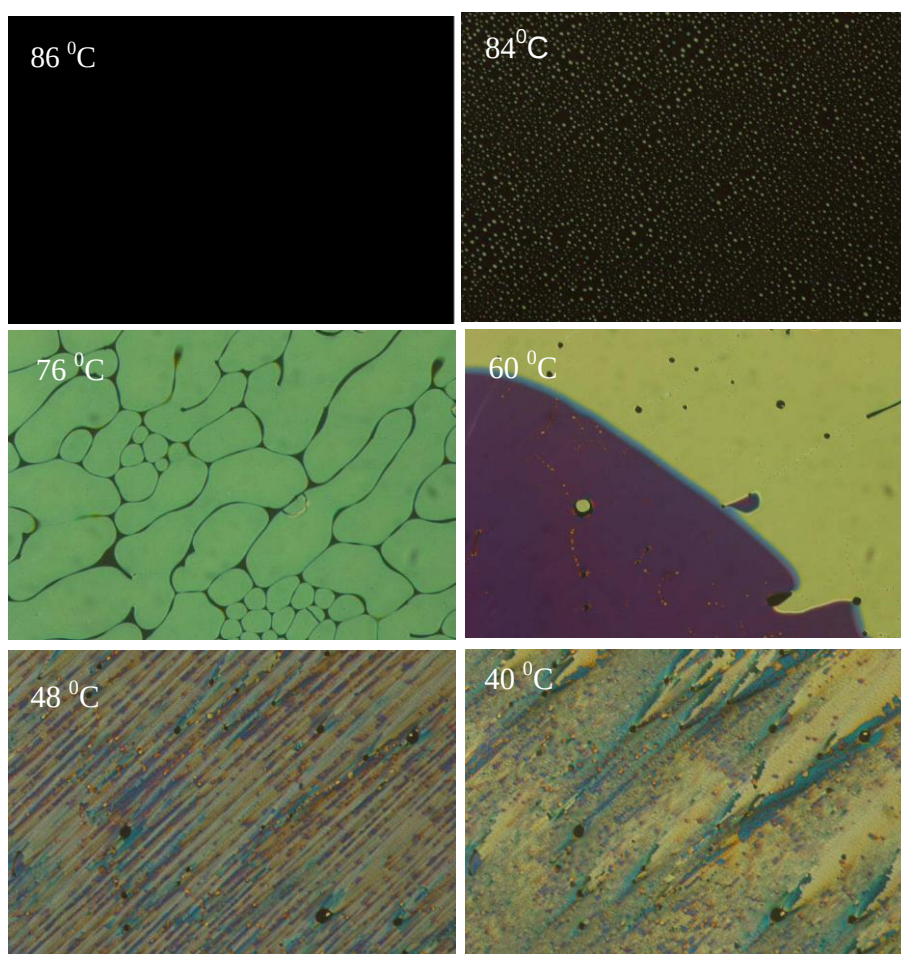


Figure 4.1 Micro textures of 0.1% SiO_2 -FLCI composite under crossed polarizers at 10X.

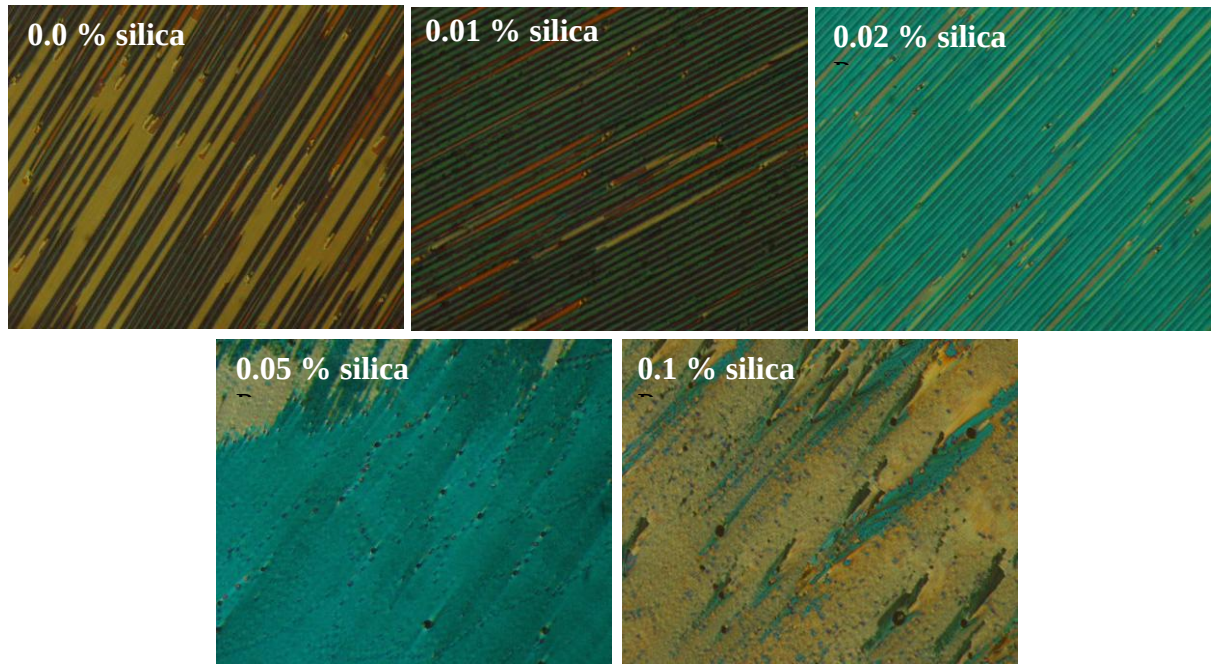


Figure 4.2 Micro textures of the various sample cells at $\Delta T = -25^\circ\text{C}$.

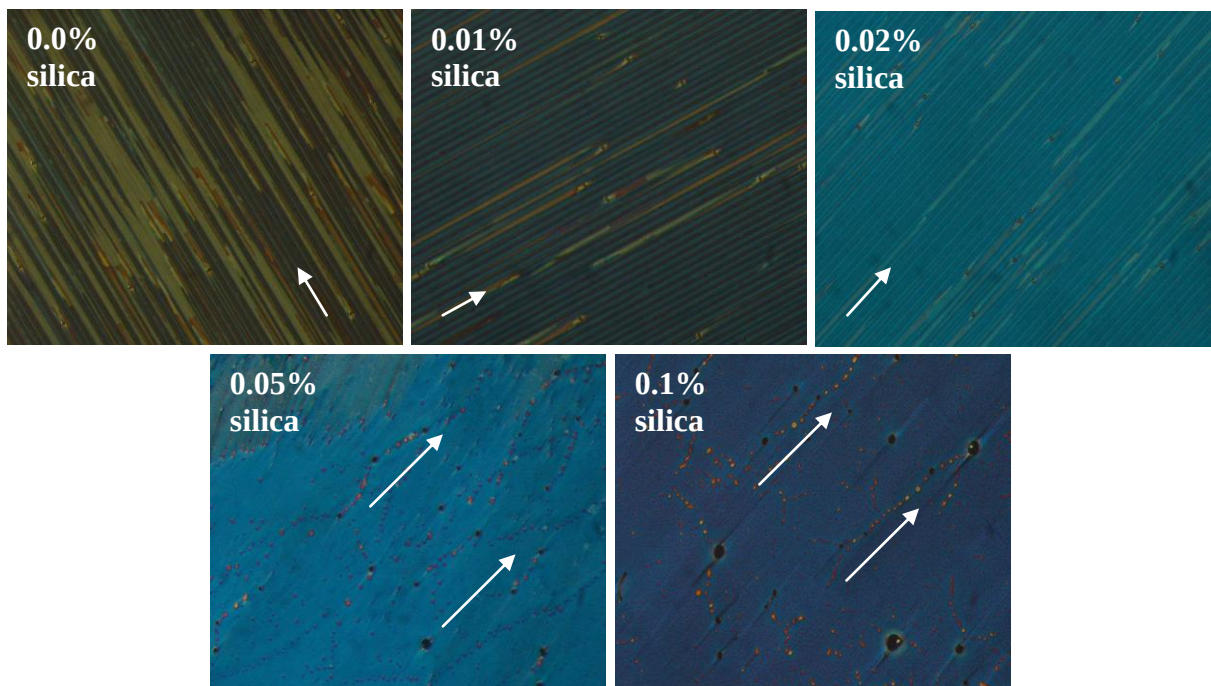


Figure 4.3 Micro textures of various samples at -5°C reduced temperature on cooling.

We observed a planer alignment in the undoped, 0.01 % and 0.02 % SiO_2 doped samples; however, alignments in 0.05 % and 0.1 % SiO_2 -doped samples were partially distorted.

Here, we noticed the growth of homeotropic domains which might have arisen due to anchoring effects introduced by the anisotropic interactions between silica-liquid crystal molecules. The alignment in lower concentrations of SiO₂ doped samples [e.g 0.01 and 0.02 %] was unhindered most likely due to the weak coupling. The heating and cooling cycles were repeated for the reproducibility of the results.

Fig.4.3 depicts the micro- textures of various samples at -5°C reduced temperature. Some chain like structures were observed in 0.05 and 0.1 wt % SiO₂ composites under the microscope. However, no such chains were seen in 0.01 and 0.02 wt % samples. It may be because of low concentrations of silica in the FLCI where interactions between nano particles and liquid crystal molecules are relatively weak. But as the SiO₂ concentration increases, anisotropic interactions between SiO₂-SiO₂ particles and SiO₂-FLC molecules become stronger and chain like structures result as reported by other research groups also [21, 23]. These results are supported by a slight increase in the isotropic temperature of SiO₂ samples, since higher temperature is required to overcome the strong interactions as compare to undoped sample.

4.4.3. Dielectric spectra

The molecular orientation and its geometry in the chiral smectic C (SmC*) phase is shown in fig.1.12 in chapter1, where θ and ϕ represents the tilt and azimuthal angle respectively. The complex dielectric permittivity in terms of real (ϵ') and imaginary (ϵ'') parts is given by the relation

$$\epsilon^*(\omega, T) = \epsilon'(\omega, T) - i \epsilon''(\omega, T) \quad (4.1)$$

where $\omega = 2\pi f$ is the angular frequency of the applied electric field and T is the working temperature. At frequencies <1 MHz, the dielectric response mainly consists of two modes in the SmC* phase (i) the goldstone mode (GM) due to azimuthal angle (ϕ) fluctuations and (ii) the soft mode (SM) due to tilt angle (θ) fluctuations [29-30]. The complex permittivity can be written as follows

$$\epsilon_{\perp}^* = \epsilon_{\infty} + \frac{\Delta \epsilon_{GM}(T)}{1 + (i\omega\tau_{GM})^{1-\alpha_{GM}}} + \frac{\Delta \epsilon_{SM}(T)}{1 + (i\omega\tau_{SM})^{1-\alpha_{SM}}} \quad (4.2)$$

where $\Delta\epsilon_{GM}$, $\Delta\epsilon_{SM}$ are the dielectric strengths of GM and SM respectively and τ_{GM} , τ_{SM} are their respective relaxation times. α_{GM} and α_{SM} represent the distribution parameters. Other

relaxation modes (e.g surface like mode, SLM and bulk domain mode, BDM) [31-32] have been also reported in FLC mixtures, thus the equation 4.2 is modified as follows

$$\varepsilon_{\perp}^* = \varepsilon_{\infty} + \frac{\Delta \varepsilon_{GM}(T)}{1 + (i\omega\tau_{GM})^{1-\alpha_{GM}}} + \frac{\Delta \varepsilon_{SM}(T)}{1 + (i\omega\tau_{SM})^{1-\alpha_{SM}}} + \frac{\Delta \varepsilon_{BDM}(T)}{1 + (i\omega\tau_{BDM})^{1-\alpha_{BDM}}} + \frac{\Delta \varepsilon_{SLM}(T)}{1 + (i\omega\tau_{SLM})^{1-\alpha_{SLM}}} \quad (4.3)$$

SLM arises due to coupling of surface domains with the field and BDM due to the interaction of bulk domains with the electric field.

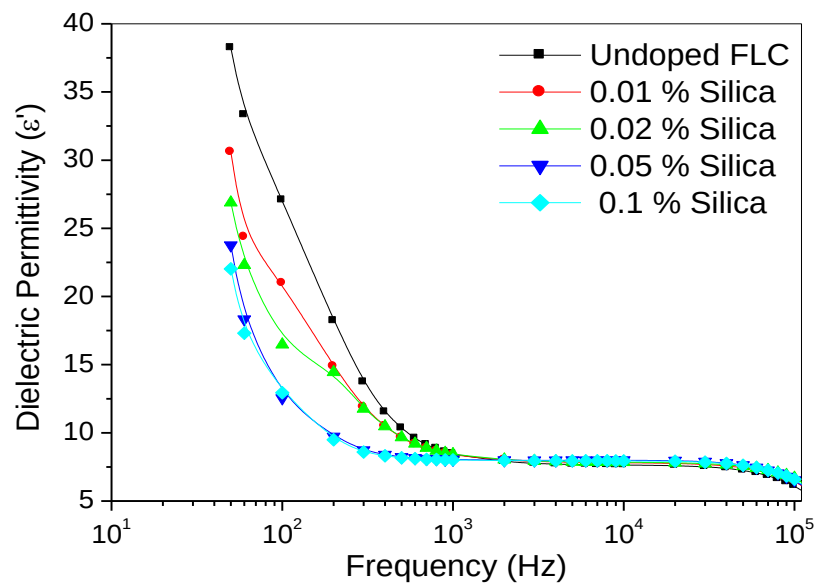


Figure 4.4 Dielectric permittivity as a function of frequency at $\Delta T = -25^{\circ}\text{C}$.

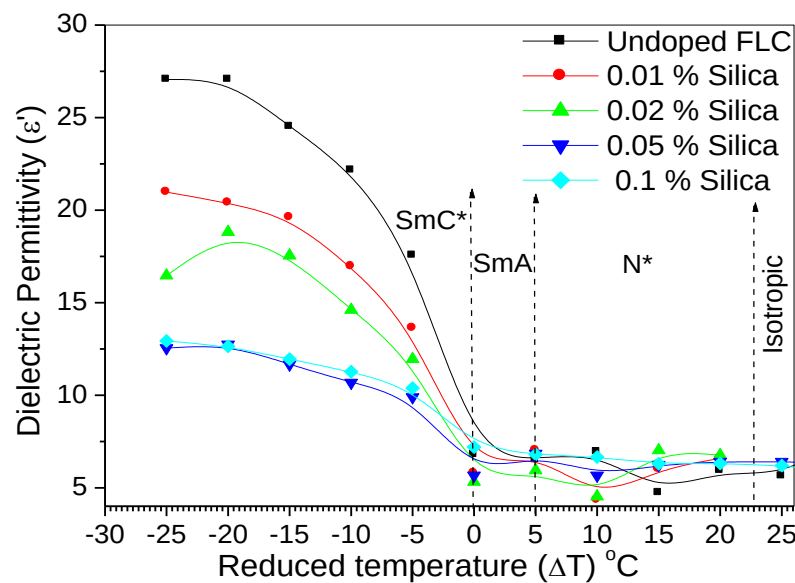


Figure 4.5 Dielectric permittivity as a function of reduced temperature at 100 Hz.

Frequency and temperature dependence of complex permittivity

Variation of dielectric permittivity (ϵ') as a function of frequency at different SiO_2 concentrations is shown in fig.4.4. We observed that the SiO_2 particles strongly influenced the dielectric spectra at low frequencies (<1 kHz), however, ϵ' didn't vary much beyond this frequency. It could be due to the fact that the response of the molecules below 1 kHz is predominantly affected by the ionic conductance (multi-component nature of the material) and the electrode polarization whereas above 1 kHz, the combined effects of lead inductance and electrode surface resistance contribute to the saturation in ϵ' . At still higher frequencies (>100 kHz), the characteristic dispersion mode due to ITO coated surface electrodes and lead inductance together contributes to lower the dielectric response of composite medium [33-36].

It was interesting to notice a gradual decrease in dielectric permittivity up to 43% for given SiO_2 doping concentration in the SmC^* phase (50Hz to 1kHz range) whereas at higher frequencies (2kHz to 100kHz), dielectric permittivity increased from ~ 1 to 1.5 % as compared to the undoped FLCI. We believe that the effective volume of the liquid crystal matrix could decrease with SiO_2 doping, thereby controlling the structure and thus the dielectric permittivity in the material [17,27,37]. Rotational viscosity etc. also contributes to this phenomenon; however, we will discuss their contributions in section 4.4.4.

The variation of dielectric permittivity (ϵ') as a function of reduced temperature for the undoped and silica doped samples is shown in the fig.4.5. The permittivity decreases near the SmC^* to SmA phase transition temperature in both the undoped and doped samples, however no variation was noticed in the other liquid crystal phases in the given sample.

Typical behaviour of the dielectric loss (ϵ'') as a function of frequency in SmC^* phase is shown in fig.4.6. Two loss peaks corresponding to low and high frequency respectively were observed, implying two relaxation modes. The first loss peak corresponds to the phase fluctuations in the azimuthal angle (goldstone mode). It decreases with increase in silica concentration in the frequency of 50 Hz to 1 kHz. We noticed that for various SiO_2 concentrations (i.e. $x = 0.01, 0.02, 0.05$ and 0.1), the decrease in losses varied from 30% to 80% as compared to the undoped sample. The decrease in the dielectric losses continues and the second loss peak appeared at about 200 kHz due to characteristic absorption mode of high resistivity ITO coated electrodes and is not related to any other mode in the liquid crystals [34]. This loss peak is increased by 1 to 3 % as the

concentration of the silica nano particles is increased from 0.01 to 0.1%. It got shifted towards the higher frequencies side. This reflects that the absorption mode due to ITO coated electrodes does not depend on the silica concentration.

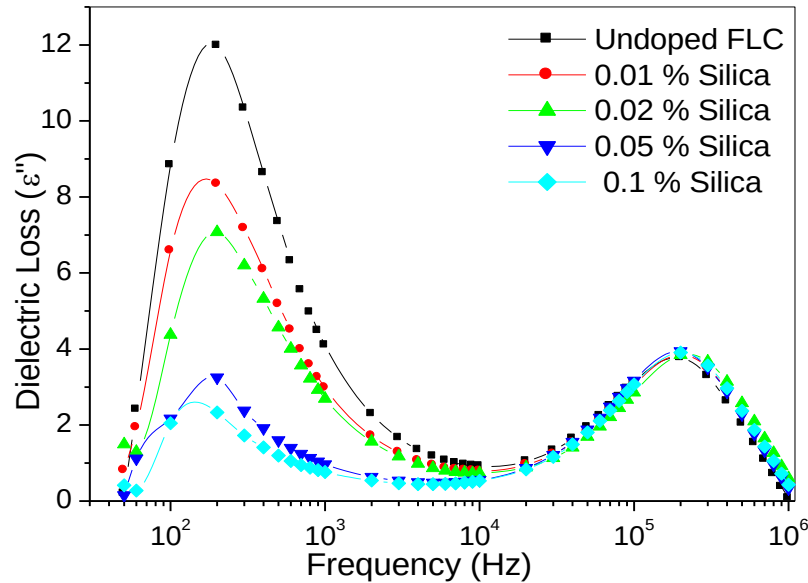


Figure 4.6 Dielectric loss as a function of field frequency at $\Delta T = -25^{\circ}\text{C}$.

The variation of dielectric permittivity and dielectric losses as a function of silica concentration at different bias voltage is shown in fig 4.7(a, b) respectively. A gradual decrease in both the parameters with increasing silica concentration (up to 0.05%) was noticed and thereafter attained saturation. This may be due to the fact that 0.05wt% silica is enough to completely disrupt the helix unwinding. Thus further increase in silica concentration to 0.1 wt% does not appreciably change the dielectric permittivity and dielectric losses and hence saturation is obtained.

Dielectric relaxations

The dielectric relaxation spectra of SiO_2 doped FLC composites in terms of Cole-Cole profile is shown in the fig.4.8. We notice that the GM relaxation was gradually suppressed with increase in silica concentration. We believe that the silica networks formed in the sample hinder the helix unwinding by electric field thereby reduces the GM contribution. The increase in rotational viscosity with increasing silica concentration could also be the cause for this variation. At $\text{SmC}^* \text{-SmA}$ transition temperature, GM disappears and the soft mode dominates. At lower frequencies, silica networks have soft

annealing character but it becomes rigid at higher frequencies thus inducing quenched disorder in the SmC* phase. The contribution of LC modes at higher frequencies was likely disturbed by ITO surface mode and has been neglected over the whole liquid crystal phase range.

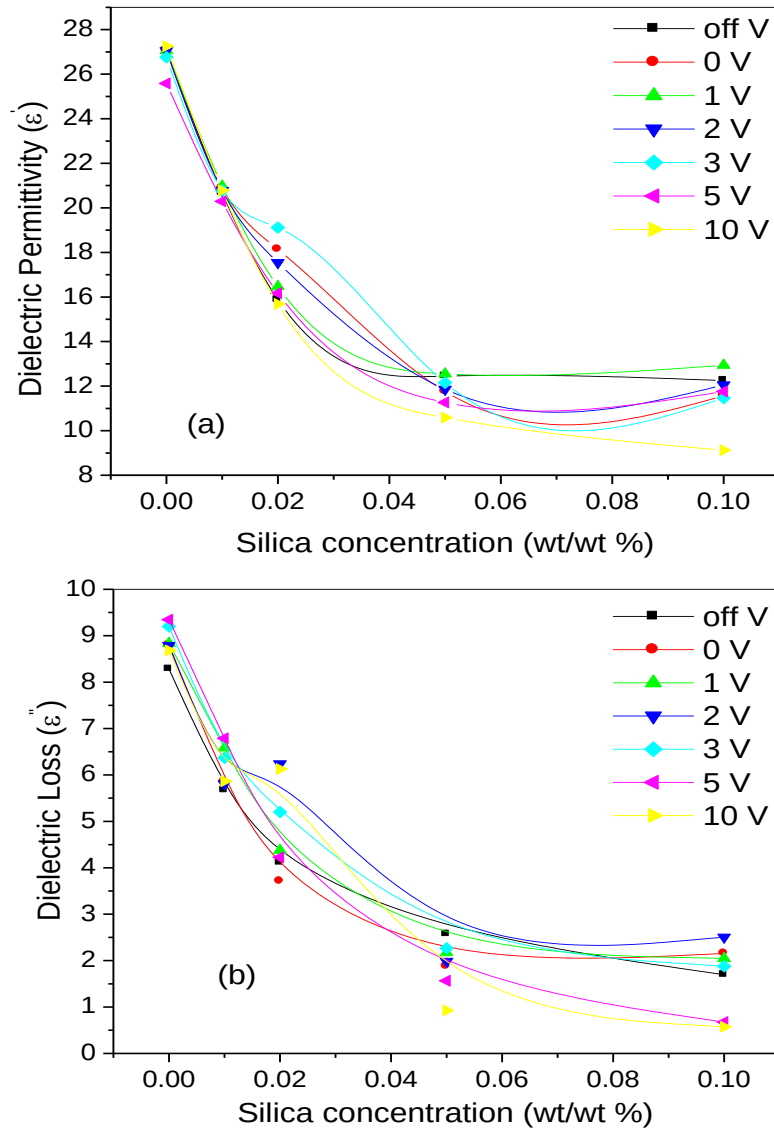


Figure 4.7 Variation of (a) dielectric permittivity and (b) dielectric loss as a function of silica concentration at different bias voltage at $\Delta T = -25^\circ\text{C}$ and 100 Hz.

Dielectric strength

The dielectric strength has been computed from the Cole-Cole plot using the following relation

$$\Delta\epsilon = \epsilon_0 - \epsilon_\infty \quad (4.4)$$

ϵ_0 and ϵ_∞ are the dielectric permittivity at static and infinite frequencies respectively [30-32]. ϵ_∞ is the high frequency dielectric constant that was obtained by intersection of semi circle with the ϵ' - axis at the higher frequency side and ϵ_0 is the low frequency dielectric constant obtained by the intersection of semi-circle with the ϵ' - axis at lower frequency.

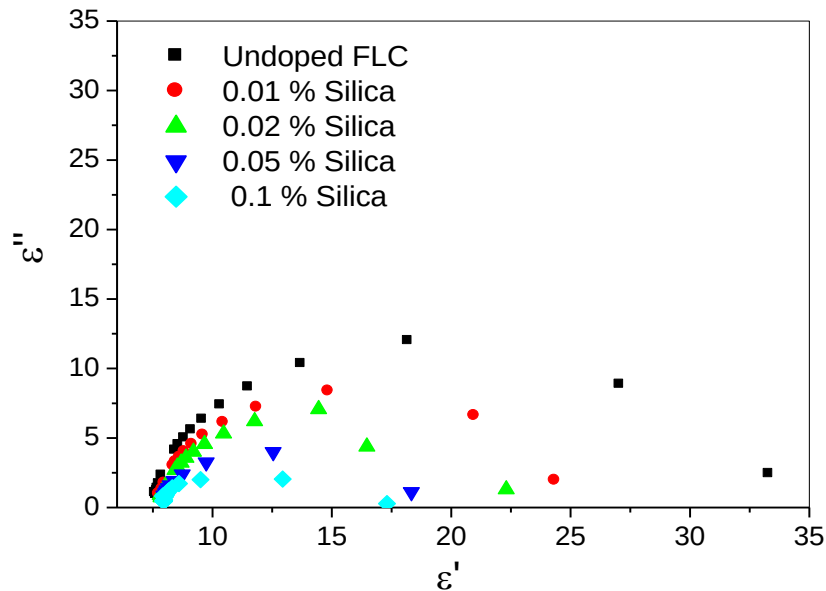


Figure 4.8 Cole – Cole profiles of the un-doped and silica doped samples at $\Delta T = -25^\circ\text{C}$.

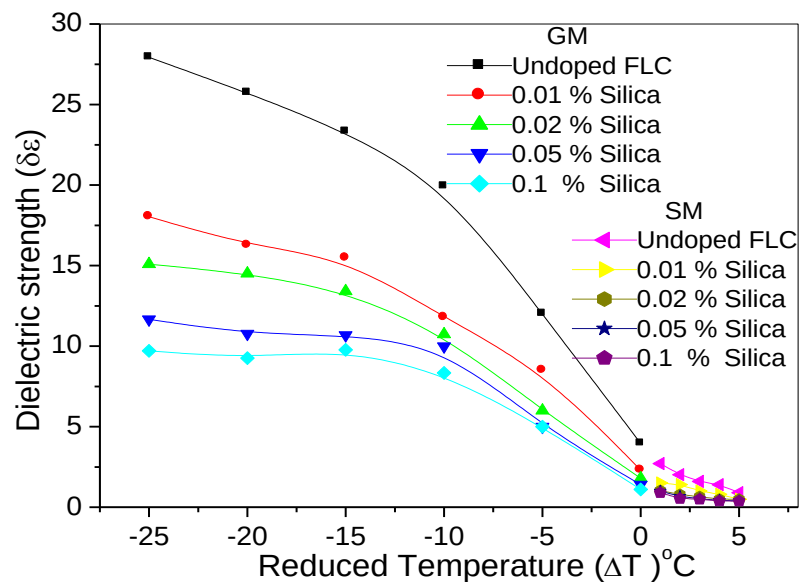


Figure 4.9: Temperature dependence of dielectric strength of GM and SM.

The dielectric strength of GM and SM as a function of temperature is shown in fig.4.9. We saw that $\delta\epsilon_{\text{GM}}$ attains maxima at lower temperatures and then decreases as we

approach the transition temperature. $\delta\epsilon_{GM}$ decreases from 36% to 66% with increasing silica concentration from 0.01 to 0.1 wt%. Similarly, $\delta\epsilon_{SM}$ decreases as the temperature approaches cholesteric phase.

Relaxation frequency

The relaxation frequency was computed by plotting $\log(v/u)$ as a function of frequency

$$v = [(\epsilon_0 - \epsilon')^2 + (\epsilon'')^2]^{1/2} \quad (4.5)$$

$$u = [(\epsilon' - \epsilon_\infty)^2 + (\epsilon'')^2]^{1/2} \quad (4.6)$$

The intercept of this line on the abscissa gives the relaxation frequency f_r of the various modes [37]. Fig.4.10 shows the variation of relaxation frequency of GM (f_{rGM}) as a function of reduced temperature. f_{rGM} increases sharply near the transition temperature. Effects of silica doping on f_{rGM} can be noticed over the whole temperature range.

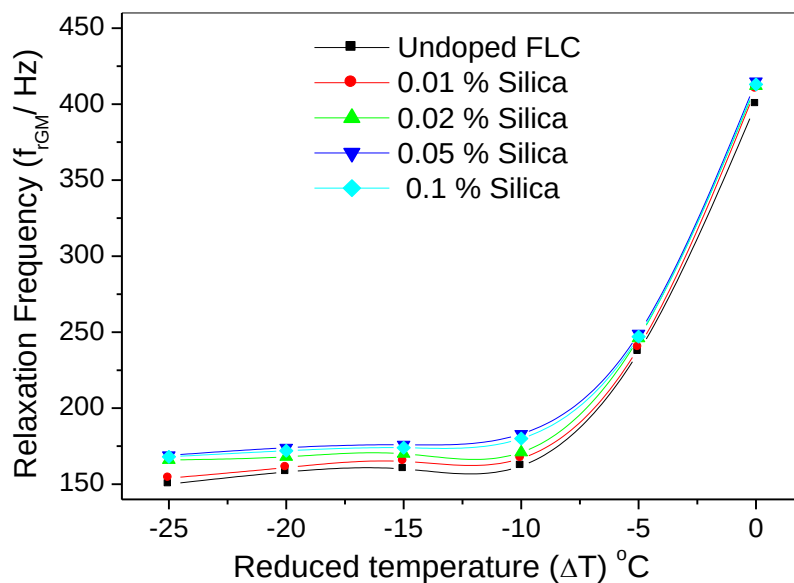


Figure 4.10 GM relaxation frequency as a function of silica concentration at 100 Hz.

4.4.4 Electro-optic studies

Spontaneous polarization

The spontaneous polarization is directly related to fraction of switching molecules and provides information about the internal structure of mesophase. The coupling of

molecular polarization (P) with electric field (E) within the smectic layers of FLC results into macroscopic polarization. With the application of an electric field, helix in the FLC unwinds, macroscopic polarization becomes non-zero and consequently, the sample gets spontaneously polarized. Polarization reversal current method is one of the well defined techniques for measuring spontaneous polarization (P_s) and switching response (τ_R) of FLC molecules [38].

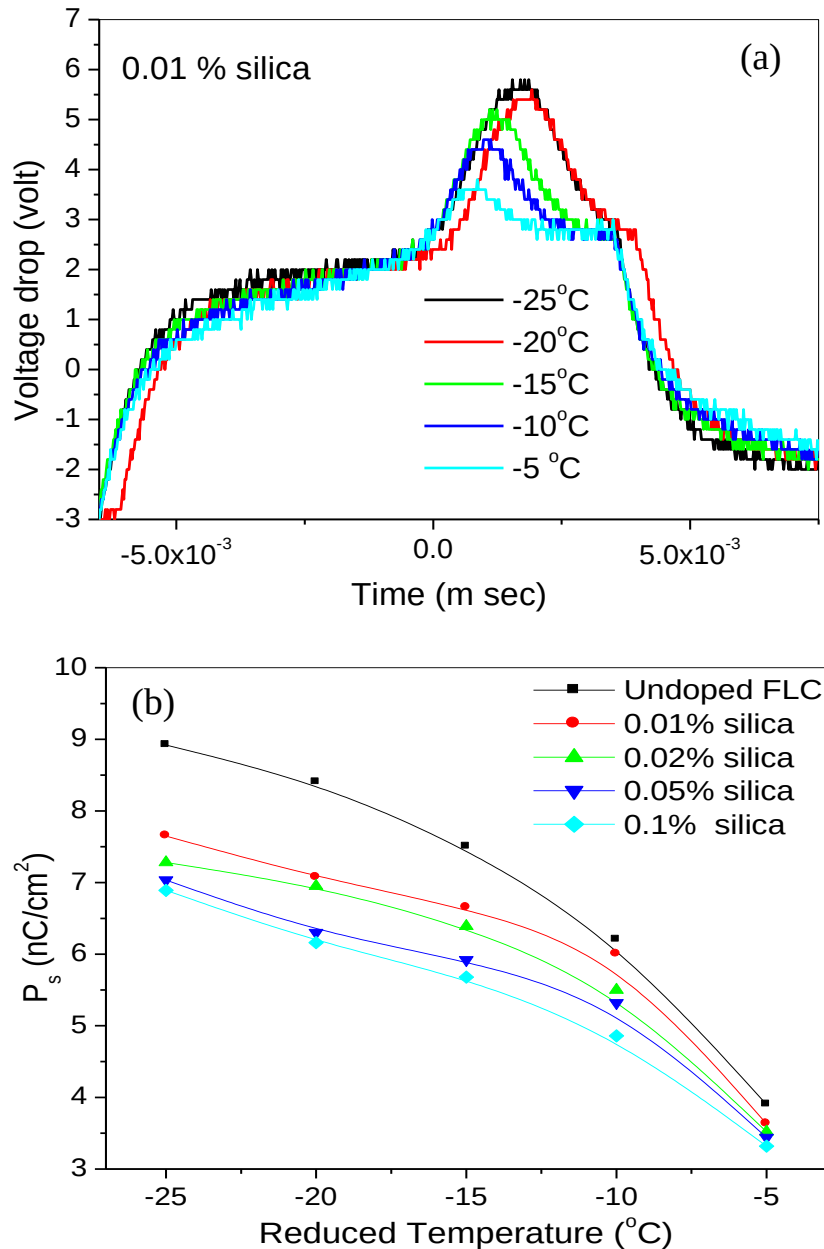


Fig.4.11 (a) Effect of temperature on polarization hump in 0.01% silica sample at 30V and (b) variation of spontaneous polarization with reduced temperature at 30V in various samples.

The molecular reorientation processes correlated to helix dynamics can be examined by applying symmetric triangular voltage across the sample using a function generator. The dipoles thus get re-oriented between two stable polarization states (Up and Down) and the molecular re-alignment can be detected on the digital storage oscilloscope in the form of voltage drop across a standard resistor [32, 37-39]. The experimental set-up and other details of this method are already reported in chapter 3 (section 3.4.3).

Fig.4.11 (a) shows the oscilloscope traces of triangular wave output at various reduced temperatures in 0.01% silica composite. Larger area under the polarization hump represents higher P_s magnitude. It can be clearly noticed that area under the polarization hump and hence P_s decreases with the increasing temperature in the ferroelectric phase. The decrease in P_s value with increase in temperature may be due to weak P-E (polarization- electric field) coupling and P- θ coupling (polarization-tilt angle) coupling. As the transition temperature T_{C^*A} approaches, polarization peak decreases sharply due to helix unwinding (increase in disorder). Decrease in P_s also reflects the second order property of chiral smectic C phase. Near T_{C^*A} , P_s is due to combined effects of electro-clinic and induced polarization. The decrease in the magnitude of P_s with increasing temperature obeys the power law given by the relation [40-41]

$$P_s = P_o(T_c - T)^\beta \quad (4.7)$$

where critical exponent $\beta = 0.5$, as predicted by mean field theory. The behaviour of calculated P_s as a function of reduced temperature for undoped FLCI and various silica composites (0.01%, 0.02%, 0.05% and 0.1 %) is shown in fig. 4.11(b). Our results indicate that silica composite with lower SiO_2 concentration (0.01%) show higher P_s ($\sim 7.65 \text{ nC/cm}^2$) than composite exhibiting higher (0.1%) silica concentration ($P_s \sim 6.89 \text{ nC/cm}^2$) at -25°C reduced temperature. However, undoped FLCI mixture possess $P_s \sim 8.92 \text{ nC/cm}^2$ (30V). Thus SiO_2 concentration affects P_s and lowers it by about 14% in 0.01% silica sample and 23% in 0.1% silica sample in comparison to undoped sample. With increase in SiO_2 concentration from 0.02, 0.05, 0.1 wt% , decrease in P_s at 30V is 5%, 8% and 10% respectively as compared to 0.01% silica sample. The decrease in P_s could be explained by considering tilt angle (θ) measurements as it is directly related to tilt angle. It was observed from the measurements that tilt angle is slightly higher in 0.01% silica sample as compared to other silica samples as shown in fig.4.12.

These results suggest that SiO_2 nanoparticles affect the FLC molecules alignment in SiO_2 -FLCI composites which may be explained on the basis of anisotropic interactions

between silica nanoparticles and LC molecules. The lower value of P_s in the silica doped samples may be due to the induced helix unwinding in the system due to orientation of FLC molecules in the preferred direction. As the silica concentration increases, the homeotropic domains (vertical alignment) introduced by silica nanoparticles causes a further decrease in the P_s value [42]. A decrease in the dielectric contribution with increasing silica concentration has been already reported in previous section that strongly supports our results of electro-optic studies [43].

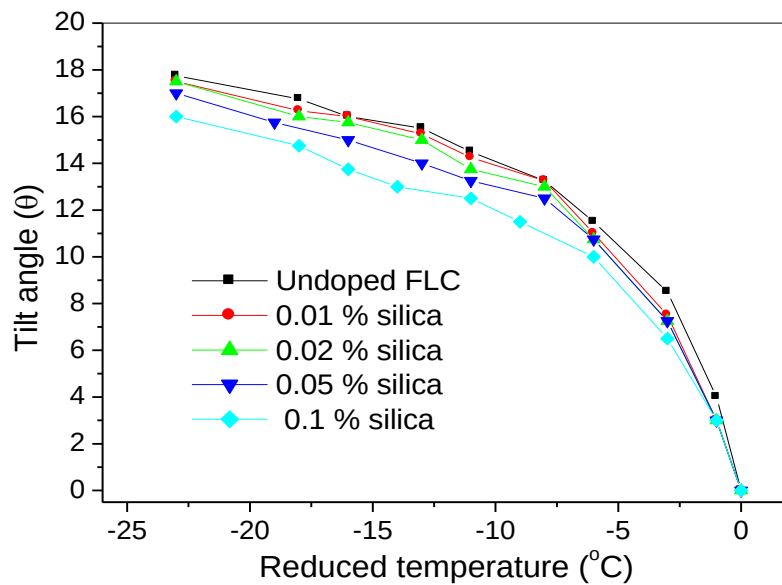


Figure 4.12 Variation of tilt angle as a function of reduced temperature in various samples.

In the presence of an external electric field, sample attains one of the two uniform states with either up or down polarization state. It develops free charges of opposite polarity on both the glass surfaces which results into depolarization field opposite to the applied electric field. Depolarization has a favorable effect (until it starts developing again) when the applied field suddenly changes its slope after each half of the cycle. This field gives rise to a small but major contribution to the overall current profile resulting in a non-linear behaviour during a linearly varying triangular wave pulse.

Fig.4.13 (a) shows the oscilloscope traces of triangular wave output obtained for 0.01 wt% silica composite at different voltage. It was observed that the height of polarization hump and hence P_s increases with increase in bias voltage due to unwinding of the helix. However, it attains a constant value at sufficiently higher bias voltage. At this stage, the molecules which were completely suppressed by the bounding plates, may transform

from uniform upward dipole state to uniform downward dipole state without attaining the zero field relaxation. Variation of P_s as a function of voltage in the various samples is illustrated in fig.4.13 (b).

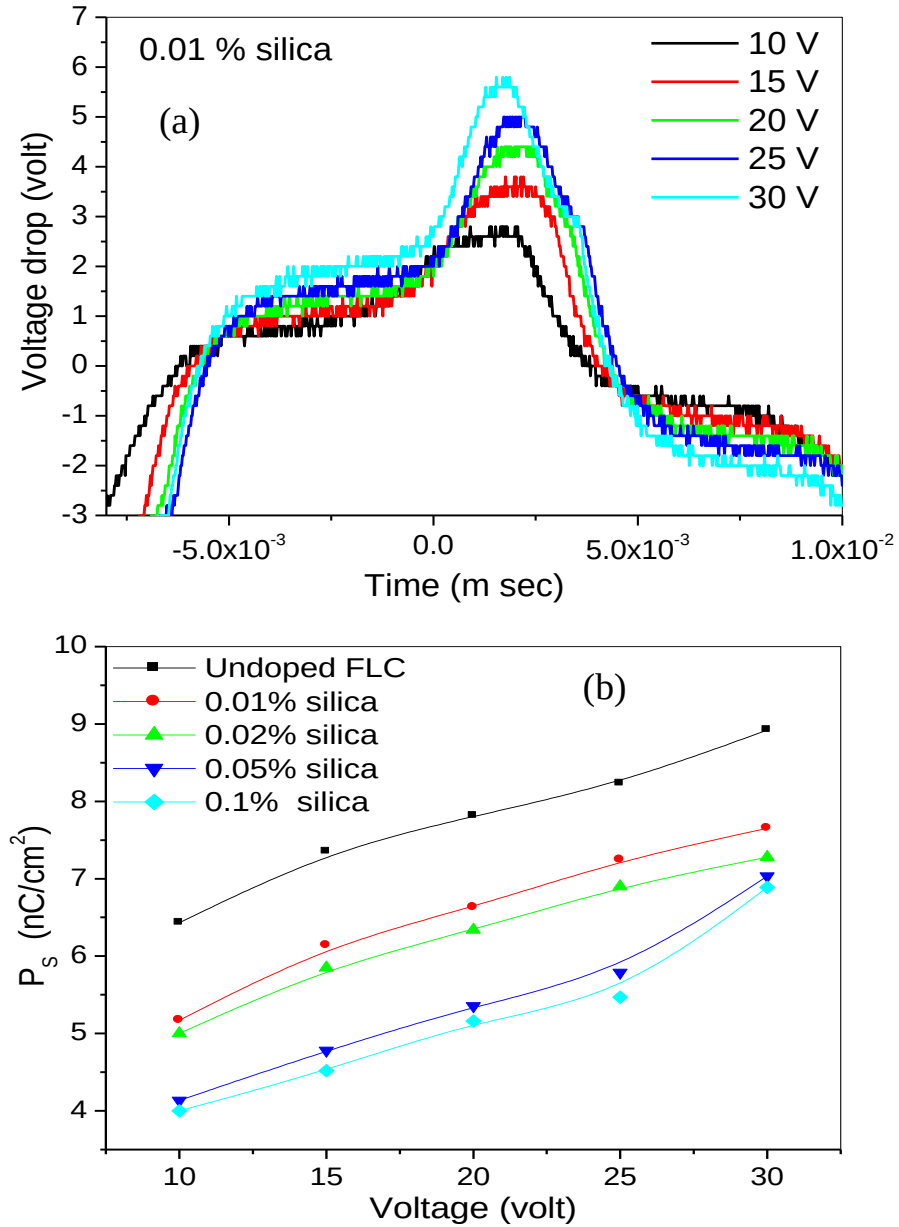


Figure 4.13 (a) Effect of voltage on polarization hump in 0.01% silica sample at -25°C and (b) Variation of spontaneous polarization with applied voltage at -25°C in various samples.

Response Time

Response time, τ_r represents the delay in time and corresponds to switching time between two stable polarization states in which average number of molecules re-orient after

applying the symmetric square wave voltage pulse at a frequency of 50Hz. FLCs offer high speed, high contrast and bi-stable electro-optic switching characteristics in a surface stabilized (SS) geometry [44]. This SS geometry of FLCs allows suppression of intrinsic helix and produces two stable states with polarization sign reversal. By applying a small external field, these states can be readily switched with a response time τ_R of few micro-second (μ sec) or milli-second (m sec). The corresponding equation of motion is described by

$$\eta \frac{\partial \phi}{\partial t} = K \frac{\partial^2 \phi}{\partial Z^2} - P_s E \sin \phi \quad (4.8)$$

where ϕ is the azimuthal angle, η is the rotational viscosity related to rotation of molecular director around the layer normal and E is amplitude of electric field. The mean elastic constant K is given by

$$K = K_2 \sin^2 \theta + K_3 \cos^2 \theta \quad (4.9)$$

K_2 and K_3 are the twist and bend elastic constants respectively and θ is the tilt angle. Eq.4.8 gives equation of motion which is due to the distribution of ϕ along the corresponding axis, caused by anchoring at both the surfaces and the chevron interface. Both the layer normal and θ do not change during the application of an electric field parallel to the layers. Thus when a small electric field is applied, the director rotates around layer normal at a constant tilt angle θ and the azimuthal angle is changed from ϕ to $\phi + \pi$ (this assumes an opposite position on the cone). This molecular reorientation can be collectively take place in the bulk (interface) and the entire macroscopic polarization P_s is then effective in the driving torque given by

$$P_s \times E = P_s E \sin \phi \quad (4.10)$$

The solution of equation (4.8) is given as

$$\phi(t) \cong 2 \tan \left[\tan \left(\frac{\phi(0)}{2} \right) \right] \exp \left(\frac{-t}{\tau_R} \right) \quad (4.11)$$

with the relaxation time,

$$\tau_R = \frac{\eta}{P_s E} \quad (4.12)$$

Eq. (4.12) gives a measure of response time τ_R of FLCI material. Here, it has been assumed that bookshelf structure appears when helix is completely unwound by external electric field. The output waveforms of square wave pulse traced on the oscilloscope for 0.01% silica sample are shown in fig.4.14 (a, b). The output of square wave gives the polarization hump which appears far away on the time scale from the square pulse edge of the applied pulse.

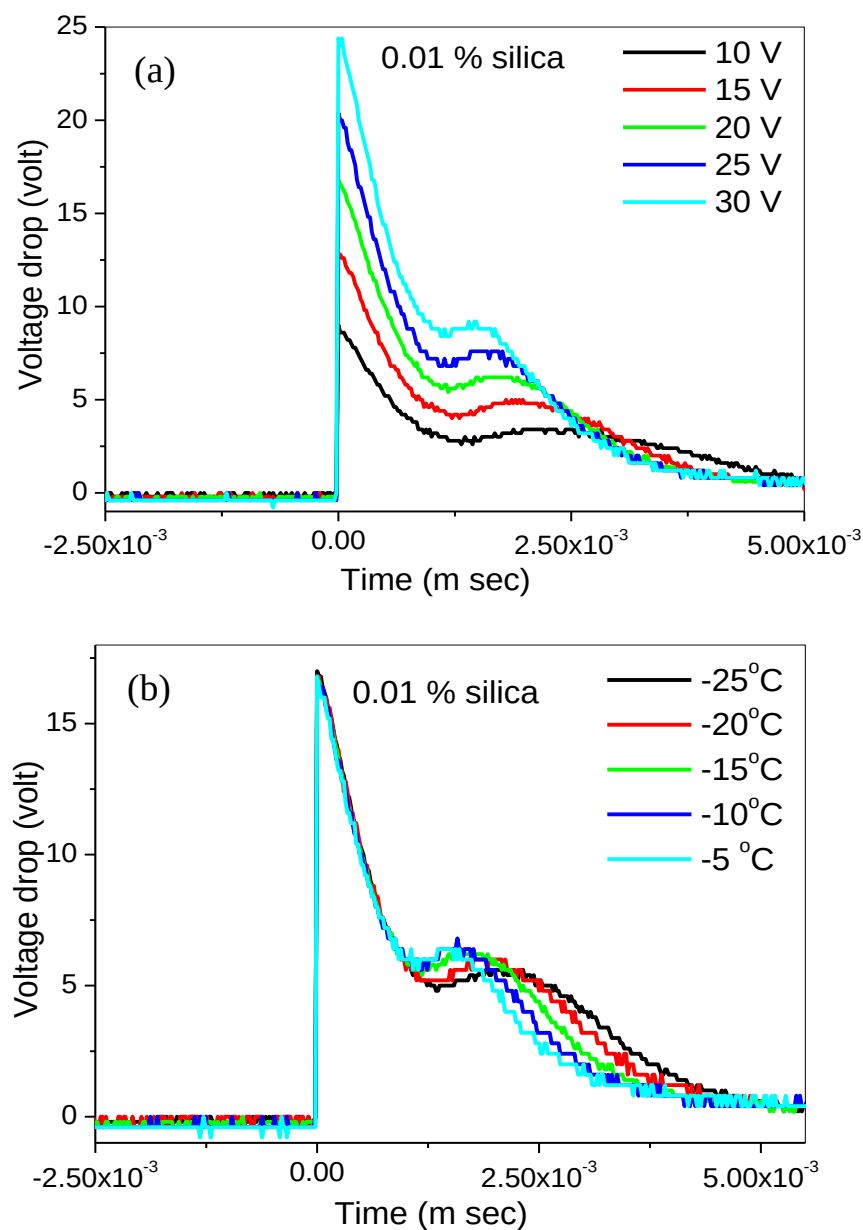


Figure 4.14 (a) Effect of voltage on switching response in 0.01% silica sample at -25°C and (b) effect of temperature on switching response at 20V in 0.01% silica sample.

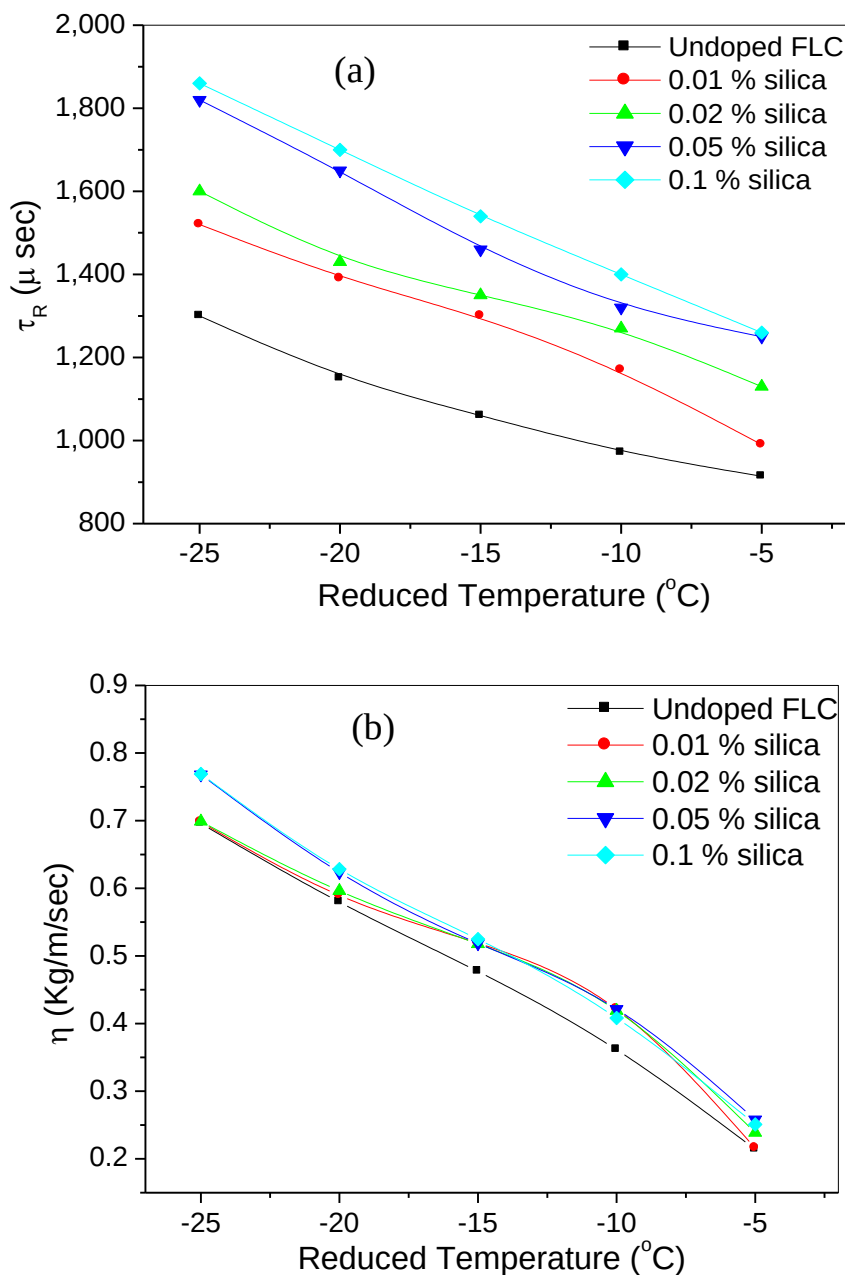


Figure 4.15 (a) Variation of response time with reduced temperature at 30V in various samples (b) Variation of rotational viscosity with reduced temperature at 30 V in various samples

We analyzed in fig.4.14 (a) that distance between polarization hump and square pulse edge decreases with increase in voltage. In other words, with increase in voltage, switching of molecules goes fast which results into decrease in response time. Similarly, as seen in fig.4.14 (b), with the increase in temperature in the ferroelectric region, fast switching of LC molecules results and hence response time decreases. The calculated

values of τ_R for various silica samples as a function of reduced temperature are shown in fig.4.15 (a). It was analyzed that 0.01 wt % silica composite have sharp response time (~ 1.52 m sec) as compared to 0.1 wt % silica composite (~ 1.86 m sec) at 30V, whereas switching time for undoped FLCI is 1.3 m sec. This may be explained on the basis of slight increase in rotational viscosity (calculated using eqn.4.12) with SiO_2 addition as shown in fig.4.15 (b). Fast switching response was depicted for low viscosity composite (0.01% silica) than high viscosity composite (0.1% silica). Since decrease in the polarization is less dominating than the increase in response time; therefore there is a net small increase in the rotational viscosity and hence the response time. Thus increase in silica concentration affects the τ_R and lowers it by 5%, 19% and 22% respectively for 0.02%, 0.05% and 0.1% silica samples as compared to 0.01% sample.

Electro-optic transmission

The optical transmission as a function of applied voltage (peak to peak) across the sample is given by [45]

$$T = \frac{I_{out}}{I_{in}} \quad (4.13)$$

I_{out} and I_{in} are the intensities of transmitted and incoming light beams through the sample respectively. The transmission of the various samples was studied by applying the symmetrical square waveform of peak to peak voltage at 50 Hz.

A typical transmission intensity profile of the electro-optic response through undoped and silica–FLCII composite samples is shown in fig.4.16. The transmission increases as a function of applied voltage up to certain value and then saturates. The sample with 0.1% doping showed highest transmission and lower threshold voltage.

Optical contrast

The electro-optic responses of various samples were measured by applying an electric field driven by a square wave pulse at 50 Hz frequency. The optical transmission results were taken on storage oscilloscope with the help of a photomultiplier tube and switching contrast ratio (CR) was calculated using the following relation

$$CR = \frac{T_s}{T_o} \quad (4.14)$$

where T_0 is the transmittance exhibited by the sample initially and T_s is the saturation value of the sample transmittance as the applied voltage increases [16].

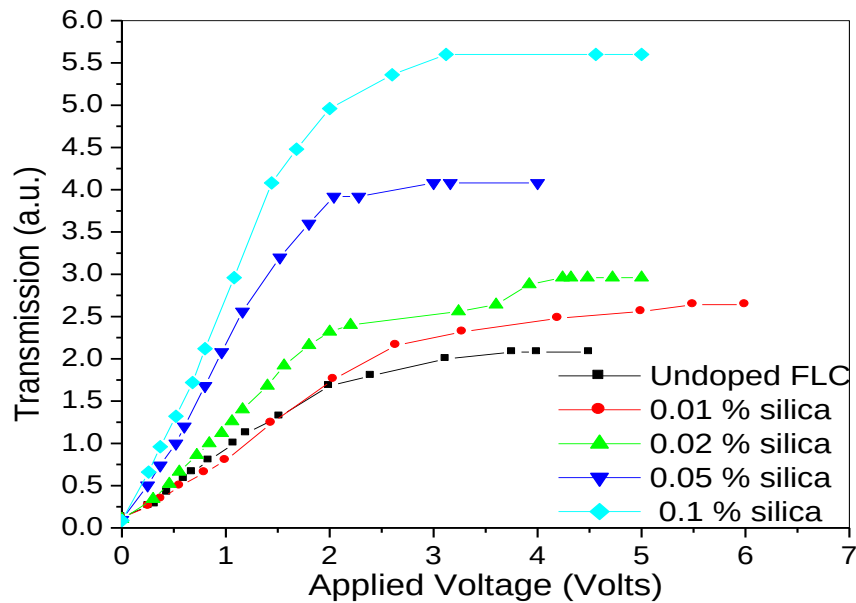


Figure 4.16 Optical transmission as a function of applied voltage at $\Delta T = -25^\circ\text{C}$.

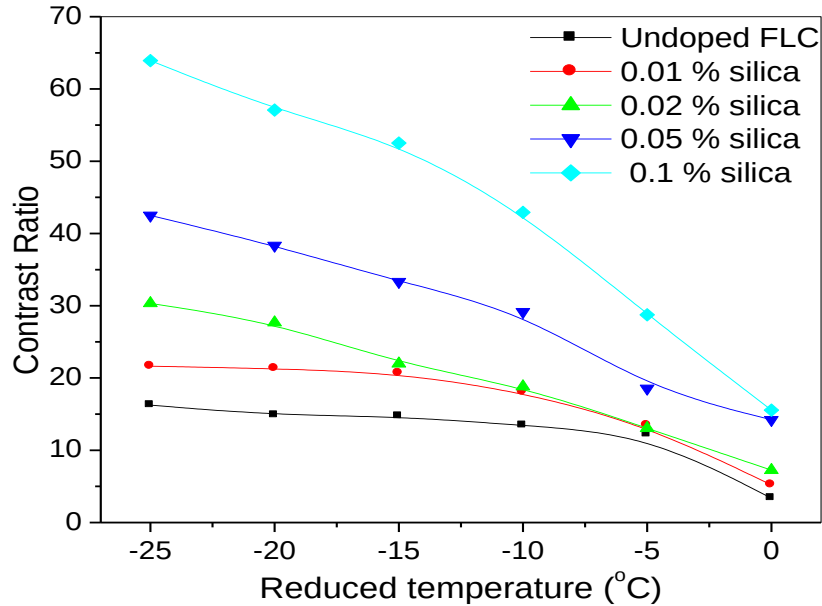


Figure 4.17 Variation of contrast ratio with reduced temperatures in various silica samples.

Electro-optic contrast is the important property of FLCs on which the performance of liquid crystal displays depends. Fig.4.17 shows the variation of CR as a function of

reduced temperature in various samples. It decreases with increase in temperature up to T_{C^*A} transition temperature. This is due to the reason that upon heating, there is an increase in the disorder of FLC molecules which in turn reduces the contrast between on and off states.

It can be seen clearly in fig.4.17 that CR increases with increase in silica concentration. Contrast ratio is respectively 16.25, 21.64, 30.33, 42.5 and 63.93 for 0%, 0.01% 0.02% and 0.1% silica doped samples. Clearly 0.1% silica sample possess 3 times more CR than undoped FLCI and about two times more than 0.01% silica sample. The micro textures of these samples show that addition of nano particles results into strong homeotropic anchoring on applying the external electric field i.e. molecules tend to align along the direction of electric field applied normal to the liquid crystal molecules which results into low scattering state of incident light [23, 27]. Thus transmission increases with increase in silica concentration and so the contrast ratio.

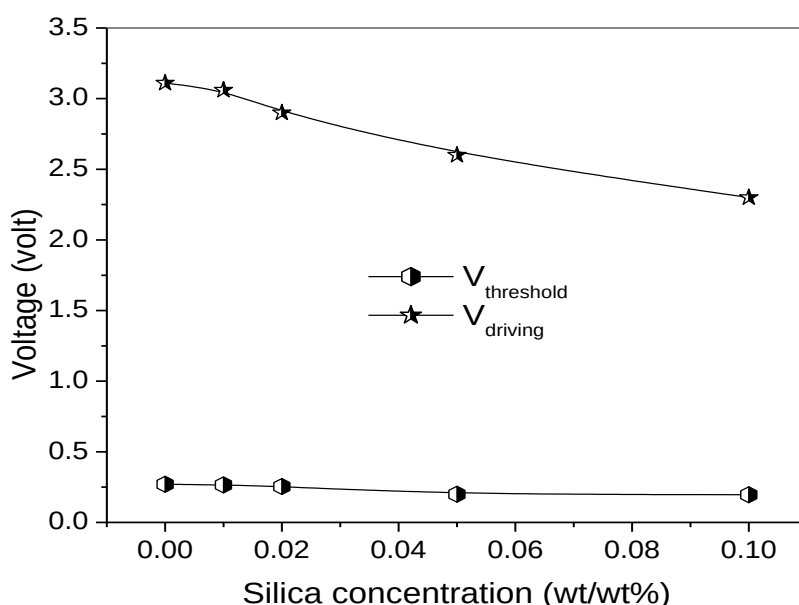


Figure 4.18 Variation of threshold voltage and driving voltage with silica concentration.

Threshold and driving voltage

A decrease in threshold voltage and driving voltage with increasing silica concentration was also observed as shown in fig.4.18. Threshold voltage is defined as the minimum applied voltage at which transmittance starts increasing sharply. Below threshold voltage, texture of liquid crystal remains undistorted. As the voltage reaches above

threshold voltage, distortion in director pattern is observed and effective birefringence (scattering) of the cell is reduced.

On the other hand, driving voltage is defined as the electric field required for the transmittance to reach 90% of saturation transmittance. There is not an appreciable decrease in threshold voltage, however driving voltage decreases more effectively with increase in silica concentration. Since the driving voltage depends upon numerous factors like cell thickness, anchoring effect etc. so its decrease with increase in silica concentration may be due to the anchoring of FLC molecules by silica nanoparticles.

REFERENCES

- 1) Chia-Wei Kuo, Shie-Chang Jeng, Hsing-Lung Wang, and Chi-Chang Liao, Appl. Phys. Lett. **91**, 141103 (2007).
- 2) A.Diaz, S. Kubo, D.H. Kwon, J. Park, D. Werner, T.Mallouk and I.C.Khoo, IEEE/LEOS Winter Topical Meeting Series, 94 (2008).
- 3) Liliana Cseh and Georg H. Mehl, J. Mater. Chem. **17**, 311 (2007).
- 4) S. Kaur, S. P. Singh, and A. M. Biradar, Amit Choudhary and K. Sreenivas, Appl. Phys. Lett. **91**, 023120 (2007).
- 5) Yu. Reznikov, O. Buchnev, O. Tereshchenko, V. Reshetnyak, A. Glushchenko, and J. West, Appl. Phys. Lett. **82**, 1917 (2003).
- 6) L. Dolgov , O. Yaroshchuk, Mol. Cryst. Liq. Cryst. **409**, 77 (2004).
- 7) Oleg V. Yaroshchuk, Leonid O. Dolgov, and Alexei D. Kiselev, Phys. Rev. E **72**, 051715 (2005).
- 8) V. Rachet, K. Lahlil, M. Berard, T. Gacoin and J. P. Boilot, J. Am. Chem. soc. **129**, 9274 (2007).
- 9) M. Kreuzer, T. Tschudi and R. Eidenschink, Appl. Phys. Lett. **62**, 1712 (1993).
- 10) N.J Diorio JR., M.R. Fisch and J.W. West, Liq. Cryst. **29**, 589 (2002).
- 11) A. Glushchenko, H. Kresse, V. Reshetnyak, YU. Reznikov and O. Yaroshchuk, Liq. Cryst. **23**, 241 (1997).
- 12) M. Bittner and M. Kreuzer, Mol. Cryst. Liq. Cryst. **282**, 373 (1996).
- 13) G. Puchkovskaya, Yu Reznikov, A. Yakubov, O. Yaroshchuk, A. Glushchenko, J. Mol. Struc. **404**, 121 (1997).
- 14) R. W. Ruhwandl and E. Terentjev, Phys. Rev. E **55**, 2958 (1997).
- 15) S. Lee and C. Park, Mol. Cryst. Liq. Cryst. **333**, 123 (1998).
- 16) Leonid O. Dolgov and Oleg V. Yaroshchuk, Colloid. Polym. Sci. **282**, 1403 (2004).
- 17) M.A. Zaki Ewiss, F. Moawia, and B. Stoll, Liq. Cryst. **34**, 127 (2007).
- 18) Chi-Yen Huang, Chien-Cheng Lai, Yao-Hsien Tseng, Ya-Ting Yang, Ching-Jui Tien and Kuang-Yao Lo, Appl. Phys. Lett. **92**, 221908 (2008).
- 19) W. Li, M. Zhu, X. Ding, B. Li, W. Huang, H. Cao, Z. Yang and H. Yang, J. Appl. Poly. Sci. **111**, 1449 (2009).

- 20) Chi-Yen Huang, Yi-Jen Huang, Yao-Hsien Tseng, *Optics Express* **17**, 20860 (2009).
- 21) Chi-Yen Huang, Chien-Cheng Lai, Yi-Jen Huang and Jian-Hong Chen, *Jap. J. Appl. Phys.* **49**, 028003 (2010).
- 22) A. Jakali, L. Alamsay, S. Borbely and L.Rosta, *Eur. Phys. J. B* **10**, 509 (1999).
- 23) S.B. Lee, K Nakayama, T. Matsui, M. Ozaki and K. Yoshino, *Proceedings of 13th international conference on dielectric liquids, Japan* 571 (1999).
- 24) S.B. Lee, K Nakayama, T. Matsui, M. Ozaki and K. Yoshino, *IEEE Transactions on Dielectrics and Electrical Insulation* **9**, 31 (2002).
- 25) Stanislaw A. Rozanski and Jan Thoen, *J. Non-Cryst. Sol.* **351**, 2802 (2005).
- 26) S.A. Rozanski and J. Thoen, *Liq. Cryst.* **32**, 331 (2005).
- 27) Z. Kutnjak, S. Kralj, S.Zumer, *Phys. Rev. E* **66**, 041702 (2002).
- 28) G. Cordoyiannis, G. Nounesis, V. Bobnar, S. Kralj and Z. Kutnjak, *Phys. Rev. Lett.* **94**, 027801 (2005).
- 29) Samriti Khosla and K.K.Raina, *J. Phy. and Chem. of Solids* **65**, 1165 (2004).
- 30) P. Malik, K.K. Raina, Alexej Bubnov and C. Prakash, *Phase Transitions* **79**, 889 (2006).
- 31) Rajbir Singh and K.K. Raina, *Int. J. of Mod. Phys. B* **22**, 2263 (2008).
- 32) Jasjit K. Ahuja and K.K. Raina, *Jpn. J. Appl. Phys.* **39**, 4076 (2000).
- 33) P. Perkowski, *Opto-Electronics Rev.* **17**, 180 (2009).
- 34) P. Perkowski, D. Łada, K. Ogrodnik, J. Rutkowska, W. Piecek, Z. Raszewski, *Opto-Electronics Rev.* **16**, 271 (2008).
- 35) M. Buivydas, F. Gouda, G. Andersson, S.T. Lagerwall, B. Stebler, J. Bömelburg, G. Heppke, B. Gestblom, *Liq. Cryst.* **23**, 723 (1997).
- 36) R. Dhar, *Indian Journal of Pure & Applied Physics* **42**, 56 (2004).
- 37) K.K. Raina and Jasjit K. Ahuja, *Mol. Cryst. Liq. Cryst.* **325**, 157 (1998).
- 38) Arvind K. Gathania, Buta Singh and Kuldeep K. Raina, *Jap. J. Appl. Phys.* **43**, 8168 (2004).
- 39) Parveen Malik, K.K. Raina and A.K. Gathania, *Thin Solid Films* **519**, 1047 (2010).
- 40) S. Wrobel, G. Cohen, D. Davidov, W.Haase, M. Marzec and M. Pfeiffer, *Ferroelectrics* **166**, 211 (1995).

- 41) Pradip Kumar Mandal, Sripada Haldar, Artsiom Lapanik, and Wolfgang Haase, Jap. J. Appl. Phys. **48**, 011501 (2009).
- 42) A. Levstik, Z. Kutnjak, C. Filipic, I. Levstik, Z. Bregar, B. Zeks and T. Carlsson, Phys. Rev. A **42**, 2204 (1990).
- 43) Neeraj and K.K. Raina, Phase Transitions, **83**, 615 (2010).
- 44) N.A. Clark, M.A. Handschy and S.T. Lagerwall, Mol. Cryst. Liq. Cryst. **94**, 213 (1983).
- 45) Pankaj Kumar and K.K. Raina, Current Applied Physics **7**, 636 (2007).

CHAPTER 5

CNTs Dispersed Ferroelectric Liquid Crystal Composites

Overview

We have prepared the multiwalled carbon nano tubes dispersed FLC composites by ultrasonication technique. The nanotubes were functionalized with –COOH group before dispersion to enhance their dispersion in the FLC. An effort has also gone in detail to investigate their FLC properties with varying concentration of multiwalled carbon nanotubes. The investigations on textures, colour switching, dielectric studies and electro-optic studies as a function of applied voltage, temperature and CNT concentration are given. This chapter illustrates the decrease in threshold voltage of molecular switching in CNT dispersed samples. The CNT dispersed FLC composite films show higher polarization and higher permittivity at low CNT concentration.

5.1 INTRODUCTION

Due to emergence of a new generation of functional materials, many research groups are associated with it to explore their potential. Carbon in nano meter size (fullerenes and carbon nano tubes) has attracted tremendous attention due to their unusual behaviours as compared to bulk material. Since the carbon nanotubes (CNTs) were discovered by a Japanese microscopist, Sumio Iijima in 1991 [1], they have been extensively used by various physicists, chemists, material scientists, biologists etc. CNTs exhibit unique electrical, mechanical and thermal properties and hold a great promise in the mechanical and electronics applications. Some of their exotic properties are: high strength to weight ratio, higher resistant to chemical attack, high surface area, high thermal conductivity etc. Now a days they are extensively used in field emission displays, sensors, actuators, batteries, field effect transistors, scanning probes microscopic tips for metrology, nano electronics, polymer matrix composites, electrode etc.

CNTs have also brought about many changes and new research opportunities in the field of liquid crystals since they have high aspect ratio (i.e. length to thickness ratio). CNTs offer better alignment (self alignment) to the liquid crystal molecules and hence improve some of their physical properties like dielectric properties, switching response and their morphological behaviour. Research in this area is throwing up numerous surprises because LCs provides an appropriate medium to control their orientations and field induced reorientations [2-4]. According to our literature review, first attempt to orientationally organize the single walled carbon nanotubes (SWCNTs) and multiwalled

carbon nanotubes (MWCNTs) by the nematic LC using various procedures was done by Michael *et al.* [5]. Other research groups have also reported the improved electro-optic responses in CNTs doped nematic liquid crystals [6-25]. A reduction in the residual dc due to ion trapping by CNTs was noticed in CNT doped twisted nematic cells which may solves the image sticking problem in conventional LCDs [8]. An electrically steered ON-OFF and OFF-ON switch and then magnetically steered switch based on CNTs doped nematic LC were demonstrated by Dierking et al. [9-10]. A detailed study showed that anisotropic nature of MWCNTs effectively improves the electro-optic properties of a nematic LC by modifying the dielectric anisotropy and viscosity of CNT-LC composites [12]. Super elongation of MWCNT aggregates in NLC medium was reported under certain threshold applied electric field. Inverse effect was observed on the field removal in both nematic and isotropic phases [16]. An increase in electrical conductivity and decrease in transmission for certain range of MWCNTs in nematic LC was measured [18]. An appreciable decrease in response time and transmittance was reported on minute doping of CNTs to nematic LC in a vertical aligned cell [19]. An increase in conductivity and significant memory effects were noticed in CNT doped nematic LCs [20]. A qualitative analysis of reorientation dynamics of liquid crystal nano tubes dispersions was also described [22]. Goncharuk et al. studied the optical transmission, electrical conductivity and microstructures of MWCNT doped NLC in detail and reported a Brownian motion of MWCNTs in nematic LC [25].

Lyotropic LC systems were also tried to disperse CNTs since the surfactants prevent CNT aggregation [26-28].

Malik et al. reported the dielectric studies of CNT doped FLC composites which demonstrate decrease in dielectric permittivity with CNT doping [29]. Arora et al. studied the dielectric and electro-optic properties of 0.01 wt% MWCNT doped FLC composite. The results show that response time is improved with CNT doping in FLC matrix whereas dielectric permittivity (both real and imaginary parts) decreases due to decrease in ion density in nano dispersions. They reported an increase in rotational viscosity and decrease in response time with CNT doping [30].

Podgornov et al. reported that an FLC material when doped with SWCNTs show a decrease in dielectric permittivity (both real and imaginary parts), spontaneous polarization, response time and rotational viscosity values. Also, no change in textures was observed after CNT doping [31].

Prakash et al. reported the decrease in response time, spontaneous polarization and viscosity in MWCNTs doped deformed helix FLC. They also depicted almost unchanged tilt angle, increase in conductivity and anchoring energy in CNT doped system [32].

Recently a detailed study on dielectric relaxation behavior of FLC-MWCNTs composites was revealed. Doping of a pure FLC material by MWCNTs in low concentration (0.03%) does not heavily affect the mesomorphic properties of the FLC material. However for 0.10 wt % concentration of the MWCNTs, the increase in permittivity has been detected probably due to the strong coupling between MWCNTs and FLC molecules [33].

From the above discussion, we found that a considerable amount of work has been carried out by many research groups focusing on the CNT dispersed nematic systems. Both SWCNTs and MWCNTs are used extensively. A few research groups have recently reported CNT dispersed FLCs [29-33]. However a clear understanding of CNT doped FLCs is still in infancy due to complexity of their smectic layers. FLCs exhibit much faster response times than nematics and that is why they are first choice in switching and optical applications (optical switches or binary optics).

In this chapter, we made an attempt to understand the dynamic responses of multiwalled carbon nanotubes (MWCNTs) dispersed FLC composite systems. We expect to get information about the mechanism of interaction of functionalized CNTs with FLC molecules and their contribution to the occurrence of relaxation modes.

5.2 CARBON NANO TUBES

Carbon nanotubes are fundamental new structures containing carbon atoms. They are members of the fullerene structural family which also includes buckyballs. Whereas buckyballs are spherical in shape, a nanotube is cylindrical with a diameter in the range of nanometers (10^{-9}m) and at least one end typically capped with a hemisphere of the buckyball structure. Their name is derived from their size since the diameter of a nanotube is of the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimeters in length. The nanotube structure consists of one or more coaxial cylinders of graphene sheet placed between two halves of a fullerene molecule (buckyball). They are synthesized using three basic techniques i.e. chemical vapour deposition, arc-discharge and laser ablation. CNTs are carbon allotropes and are classified into two type i.e. single walled carbon naotubes and multiwalled carbon nanotubes [34-35].

Single-walled nanotubes

A single wall carbon nanotube (SWCNT) is a one-atom thick sheet of graphite (called graphene) rolled up into a seamless cylinder. They have diameter of the order of one nanometer and a tube length of many thousands of times longer. Single-walled nanotubes are a very important variety of carbon nanotube because they exhibit important electric properties that are not shared by the multi-walled carbon nanotube (MWCNT) variants. SWCNTs are the most likely candidate for miniaturizing electronics past the micro electromechanical scale that is currently the basis of modern electronics. The most basic building block of these systems is the electric wire, and SWCNTs can be excellent conductors [36]. One useful application of SWNTs is in the development of the first intramolecular field effect transistors (FETs).

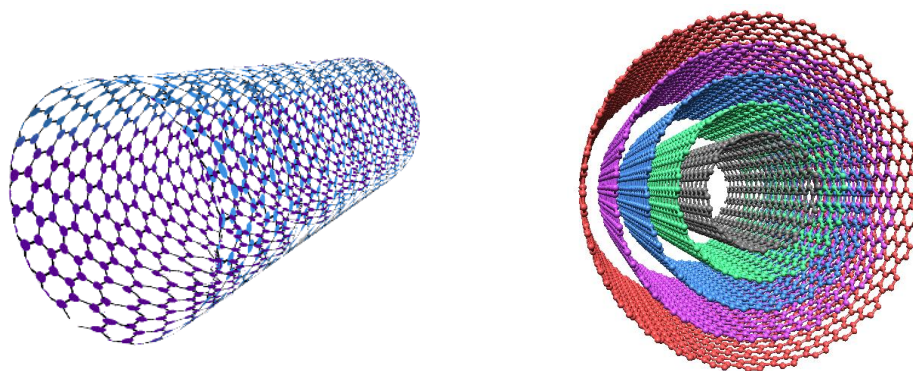


Figure 5.1 Structure of (a) single walled carbon nanotube and (b) multiwalled carbon nanotube [37-38].

Multi-Walled Nanotubes

Multi-walled carbon nanotubes (MWCNTs) are made of multiple layers of graphite rolled to form a tube shape. There are two models which can be used to describe the structures of multi-walled nanotubes. In the Russian Doll model, sheets of graphite are arranged in concentric cylinders. In the Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled up newspaper. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite (~ 3.3 Å). The MWCNTs are preferred over SWCNTs since they are less expensive and are more chemical resistant than SWCNTs. This is especially important when functionalization is required (this means grafting of chemical functions at the

surface of the nanotubes) to add new properties to the CNTs. In the case of SWCNTs, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical and electrical properties [39-41].

5.2.1 Properties based applications of CNTs

The strength of the sp^2 carbon-carbon bonds gives carbon nanotubes amazing mechanical properties. The stiffness of a material is measured in terms of its Young's modulus, the rate of change of stress with applied strain. The Young's modulus of the best nanotubes can be as high as 1000 GPa which is approximately 5x higher than steel. The tensile strength or breaking strain of nanotubes can be up to 63 GPa, that is around 50x higher than steel. These properties coupled with the lightness of carbon nanotubes give them great potential in applications such as aerospace. It has even been suggested that nanotubes could be used in the "space elevator", an Earth-to-space cable first proposed by Arthur C. Clarke. The electronic properties of carbon nanotubes are also extraordinary. Especially notable is the fact that nanotubes can be metallic or semiconducting depending on their structure. Thus, some nanotubes have conductivities higher than that of copper, while others behave more like silicon. There is great interest in the possibility of constructing nanoscale electronic devices from nanotubes and some progress is being made in this area. However, in order to construct a useful device we would need to arrange many thousands of nanotubes in a defined pattern, and we do not yet have the degree of control necessary to achieve this [34-41].

5.2.2 Functionalization of CNTs

A uniform and well dispersion of CNTs in a LC matrix is not easy since they have strong tendency to form aggregates due to the strong anisotropic interactions between them. This interaction is fundamental and well known for colloids dispersed in liquid crystals. When suspended in a liquid crystal, an attractive force between filler materials arises due to the anisotropic effects. A well homogenous dispersion of CNTs within a supporting matrix is crucial for fabricating the CNT-LC composites with enhanced properties. It is possible either by mechanically shaking or chemical functionalization. The mechanical shaking involves physical separation of the CNTs from each other whereas functionalization involves the chemical treatment of the tube surface. However, in certain cases, chemical treatment may lead to the key nanotube properties being

compromised. In general, the functionalization of CNTs requires chemical modifications of their surface supported by the mechanical shaking by ultrasonication.

MWCNTs obtained from M/S Sigma Aldrich (chapter 3) were covalently functionalized with –COOH group for better chemical stability of nanotubes in organic LCs and uniform dispersion. The chemically oxidized CNTs modify the interfacial adhesion between LC molecules and CNTs [42].

Technique used for functionalization

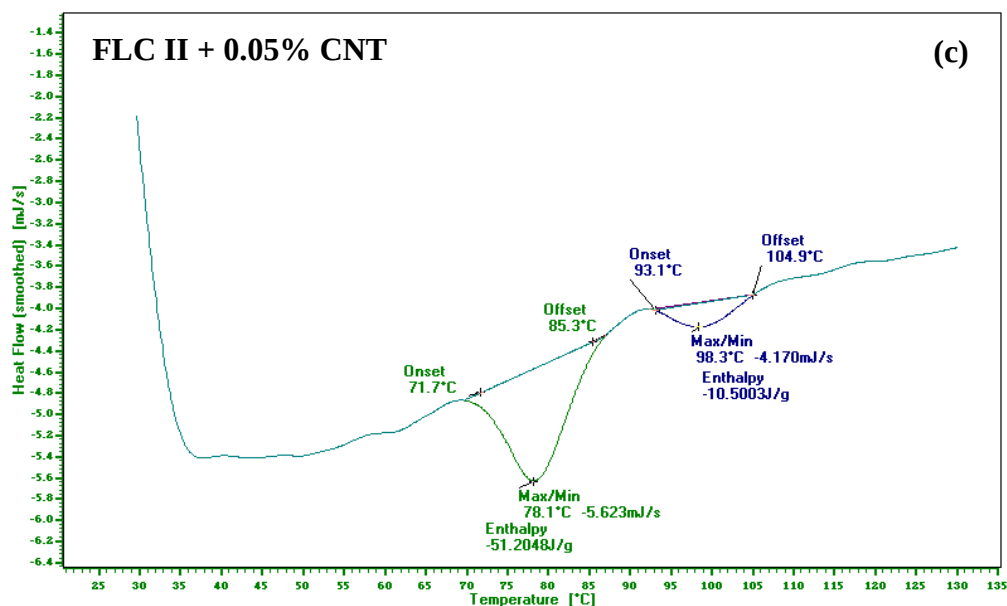
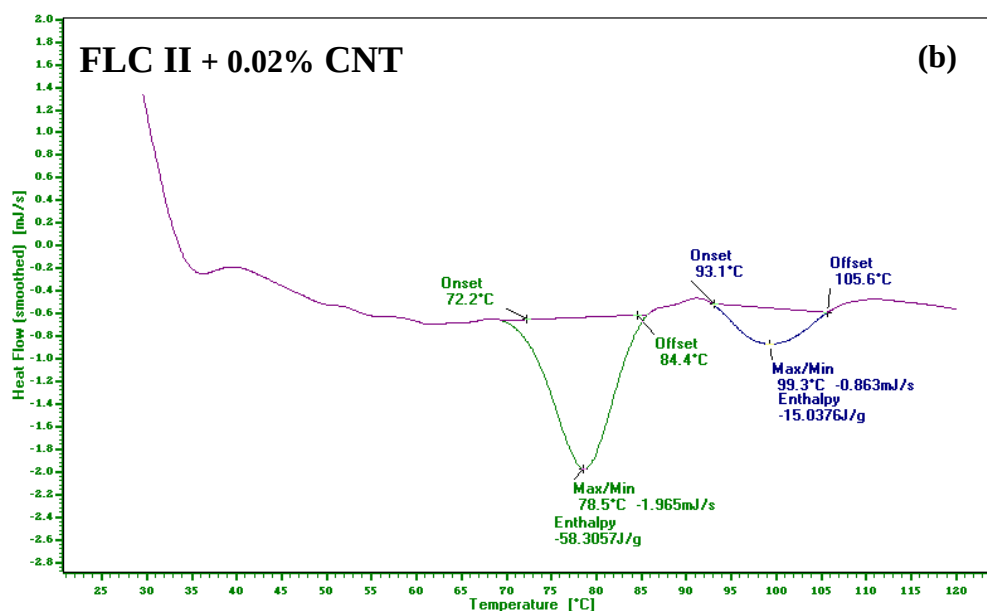
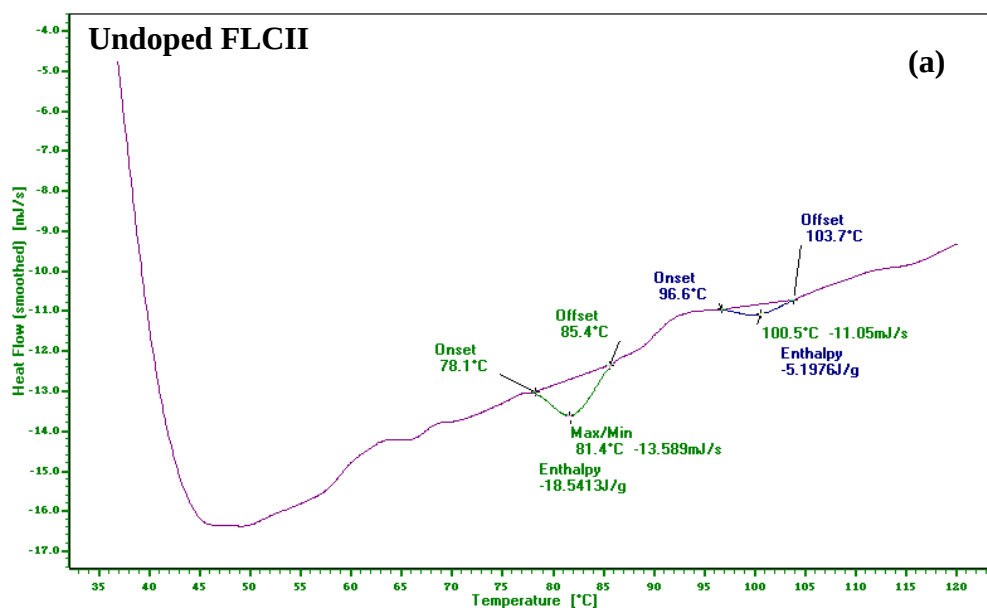
The MWCNTs (37.88 mg) were chemically functionalized by ultrasonification in a mixture of 3M of concentrated sulphuric acid and 1M of concentrated nitric acid (3:1) for 2hr at 50°C temperature, finally 1M HCL was added and mixture sonicated for ½ h at 50°C. After the completion of reaction, the mixture was diluted with deionised water and then vacuum-filtered through a polycarbonate membrane. After filtration the acid-oxidized MWCNTs were washed with deionised water in order to obtain pH value around 7 and then dried at 60°C for 12h. These acid treatments may shorten the length of the MWNT and introduce carboxylic acid groups. Oxidation disrupts the π bonding symmetry of the sp^2 hybridize carbon atoms and therefore leads to numerous side defects along the entire length of CNTs. Oxidized CNTs (carboxylic groups are dominant, therefore the CNT-COOH abbreviation is used to refer to oxidized nanotubes) remain stable in aqueous solvent for months. Further the functionalized CNTs were characterised by FTIR to confirm the functionalization.

5.3 RESULTS AND DISCUSSION

The functionalized CNTs were dispersed in the FLCII matrix in different wt/wt% (0.02, 0.05 and 0.1) and the following results were obtained.

5.3.1 Thermo-optic studies

FLCII material possesses different temperature range of ferroelectric (SmC^*) and chiral nematic (N^*) liquid crystal phases under heating and cooling conditions. The phase transition temperatures of various samples observed on heating the samples through differential scanning calorimetry are shown in fig.5.2 and were confirmed by thermal polarizing microscopy. The peaks of the phase transition in DSC curves of films agreed well with thermal polarizing microscopy observations.



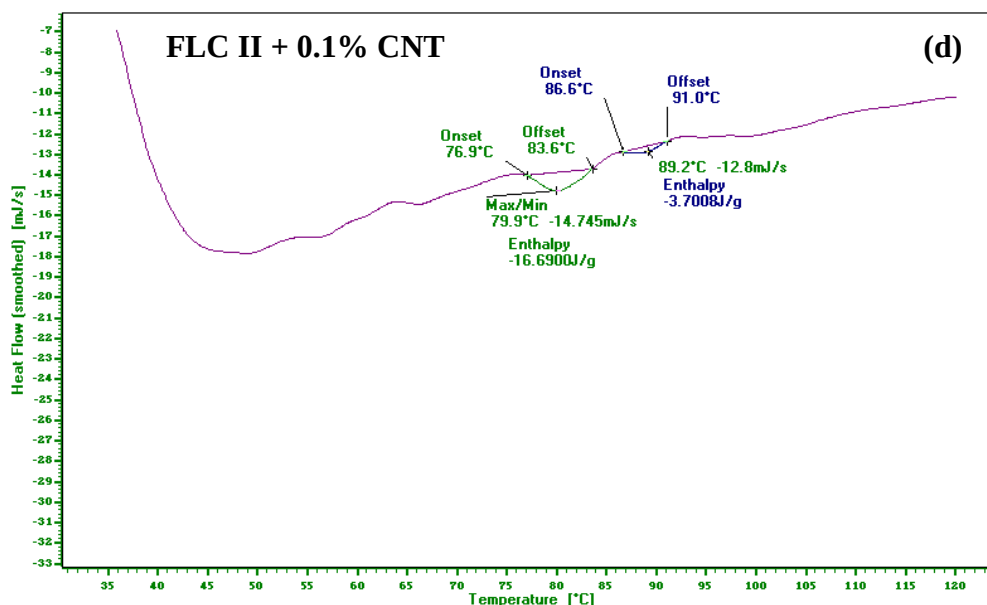


Figure 5.2 DSC profiles of undoped FLCII (a) and CNT doped FLCII (b, c &d) composites on heating the sample.

A wide range of SmC* phase was observed on cooling the sample from isotropic temperature using hot stage polarizing microscopy. The phase transition temperatures of various CNT-FLCII composites obtained during cooling the samples from isotropic temperature are given in Table 5.1.

Table 5.1: Phase transition temperatures of various samples on cooling

FLC II + CNT (wt %)	$T_I - T_{N^*}$ ($^{\circ}\text{C}$)	$T_{N^*} - T_{\text{SmC}^*}$ ($^{\circ}\text{C}$)
0.00	105.0	98.0
0.02	103.6	96.8
0.05	102.8	95.5
0.10	102.0	95.0

The influence of CNTs is clearly reflected by change in the transition temperatures. We noticed that the dispersion of 0.02% CNT has lowered the isotropic transition temperature (T_I) from 105 $^{\circ}\text{C}$ to 103.6 $^{\circ}\text{C}$ which continued to decrease with further increase in the CNT concentration. The transition temperatures are well defined and similar behaviour was found at other compositions. A CNT concentration dependence of the various transition temperatures is shown in fig.5.3.

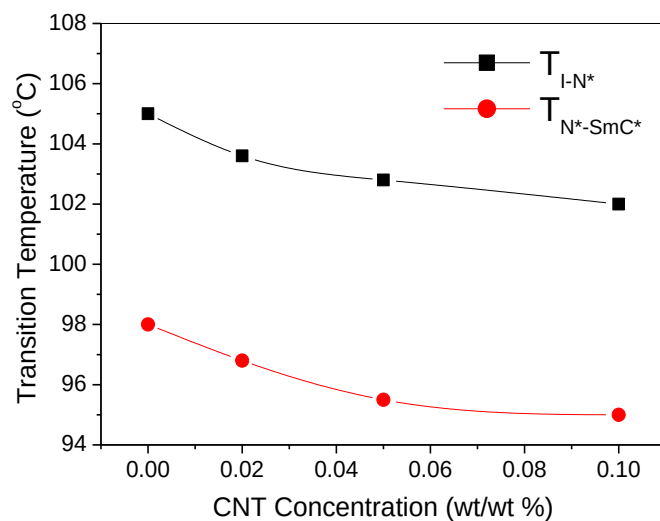


Figure 5.3 Transition temperature variations of various phases as a function of CNT concentration on cooling the samples from their isotropic temperature.

5.3.2 Switching responses in micro-textures

The LC textures were observed under optical microscope at 10X magnification for various samples.

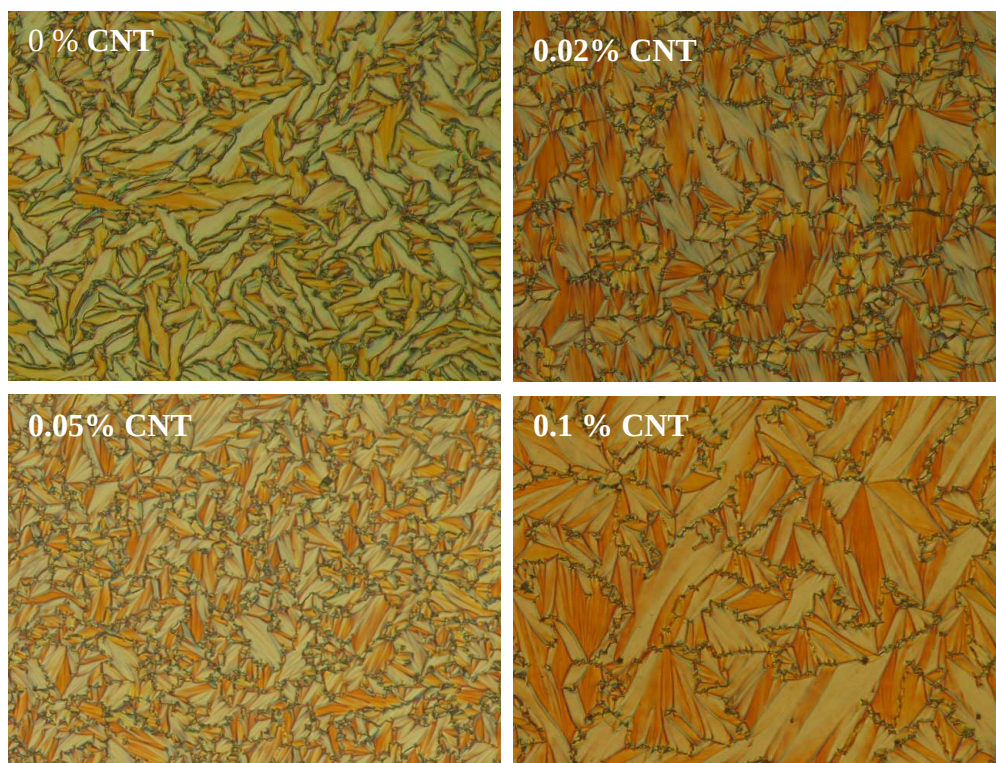


Figure 5.4 Micro-textures of undoped and CNT doped samples in SmC* phase on cooling.

No significant difference in the textures of undoped and doped samples was observed (fig.5.4). It means that small concentration of CNTs added to FLC material does not disturb the molecular orientation of LC material.

Textural changes were noticed after switching the molecules in 0.02% CNT-FLCII composite in the presence of an applied electric field as shown in fig.5.5. A change in colour with applied voltage could be clearly depicted here which points towards the presence of colour switching in the composite.

This colour switching is however present in all the CNT-FLCII composites as well as in undoped FLCII and can be clearly examined in the fig. 5.6. But somehow, the threshold voltage for switching the molecules is decreased by about 1 volt in 0.02% and 0.05% CNT composites as compared to undoped FLCII and 0.1% CNT composite.

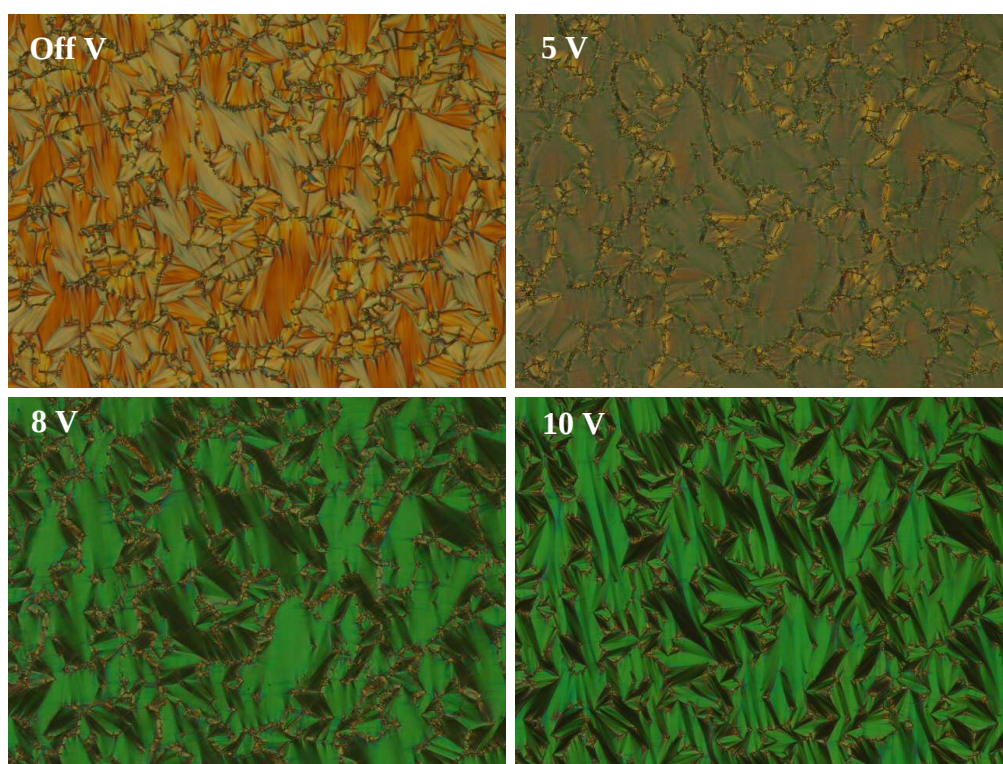


Figure 5.5 Switching responses of 0.02 % CNT-FLCII composite in presence of an electric field.

Fig. 5.7 shows the variation of threshold voltage for switching as a function of CNT concentration. It predicts that with the increase in CNT concentration, threshold value increases. However, undoped FLCII and 0.1% CNT-FLCII composite have the same value of switching threshold voltage ($1.40\text{V}/\mu\text{m}$).

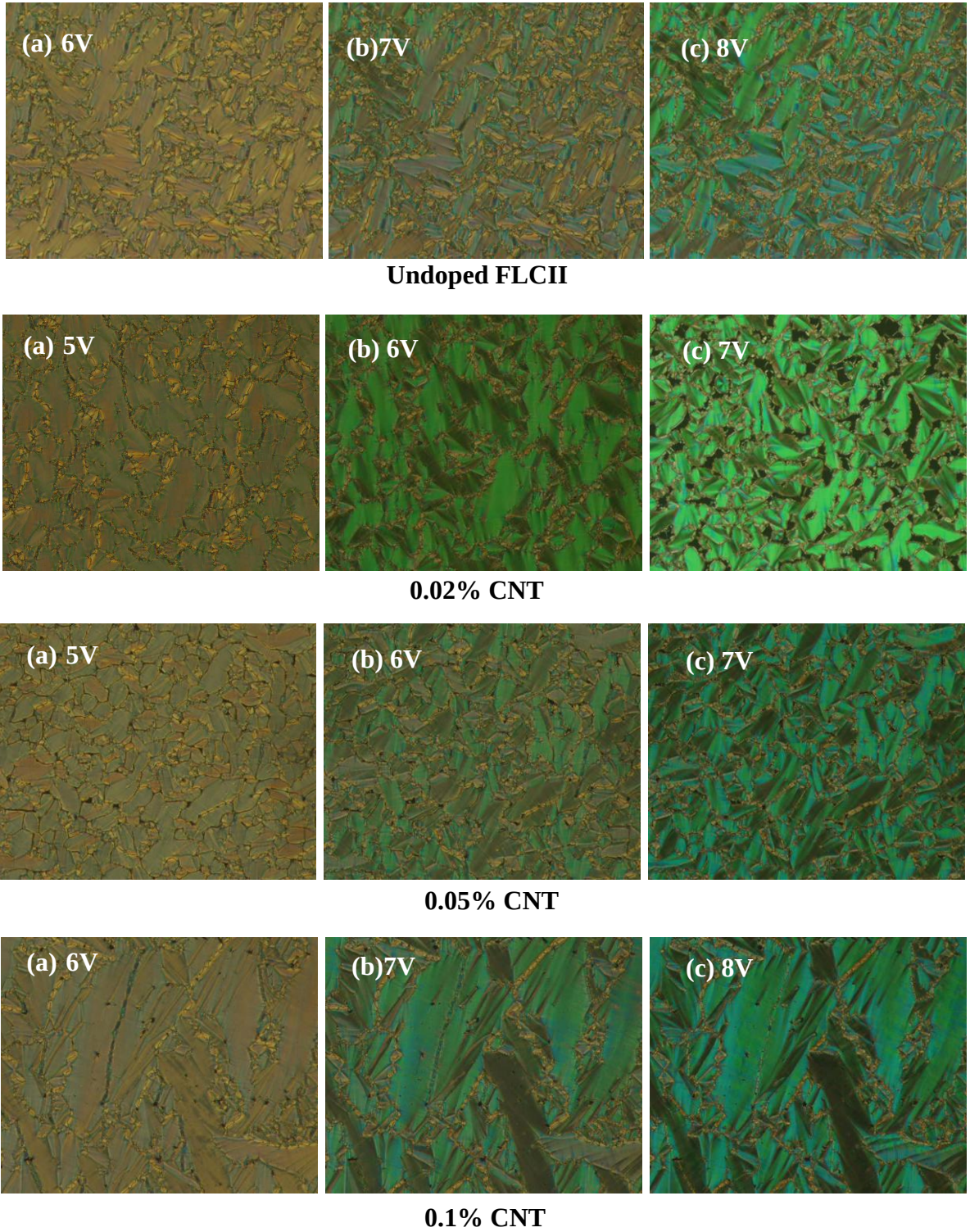


Figure 5.6 Switching responses of various CNT-FLCII composites in presence of an electric field for green colour.

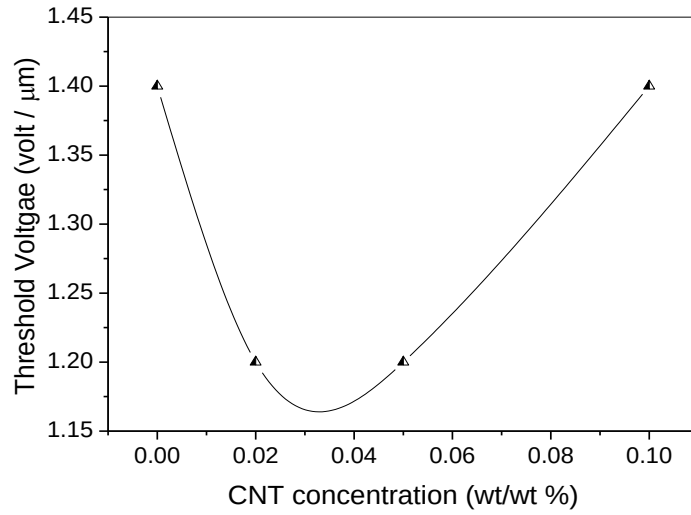


Figure 5.7 Variation of switching voltage for green colour as a function of CNT concentration.

5.3.3 Dynamic responses and dielectric spectroscopy

Dielectric spectroscopy provides information about the collective and non-collective excitation of the molecules. Besides this, two additional collective relaxation processes due to fluctuations of azimuthal angle (φ) i.e. goldstone mode (GM) and tilt angle (θ) i.e. soft mode (SM) are present. GM is formed due to helical structure in the SmC* phase. It is influenced and deformed by surface interactions, causing a substantial change in the dynamics of GM. The complex permittivity ε^* is given by

$$\varepsilon^*(\omega, T) = \varepsilon'(\omega, T) - i \varepsilon''(\omega, T) \quad (5.1)$$

where ε' and ε'' are real and imaginary parts of the complex permittivity.

Dielectric permittivity and dielectric loss

The variation of permittivity as a function of frequency in CNT-FLCII composites is shown in fig.5.8 (a). We observed that permittivity increased by about 20 to 40 % in the low frequency range (50 Hz to 1 kHz) after dispersion of CNTs. This may be due to strong coupling between CNTs which tend to align the FLC molecules by strong anisotropic interactions and hence increases the permittivity. Due to functionalization (e.g. -COOH group) the polar groups present in the CNTs and polar LC molecules results

into improved coupling and stability of CNTs with LCs [42]. However at high CNT concentrations, permittivity falls likely due to higher conducting nature of CNTs and their agglomeration. At lower CNT concentrations, we believe that both the systems mixed well and contribute to increase the permittivity of CNT-FLCII composites. Above 2 kHz frequency, permittivity was found to be independent of CNT addition. Variation in the dielectric permittivity as a function of CNT concentration is clearly seen in fig.5.8 (b).

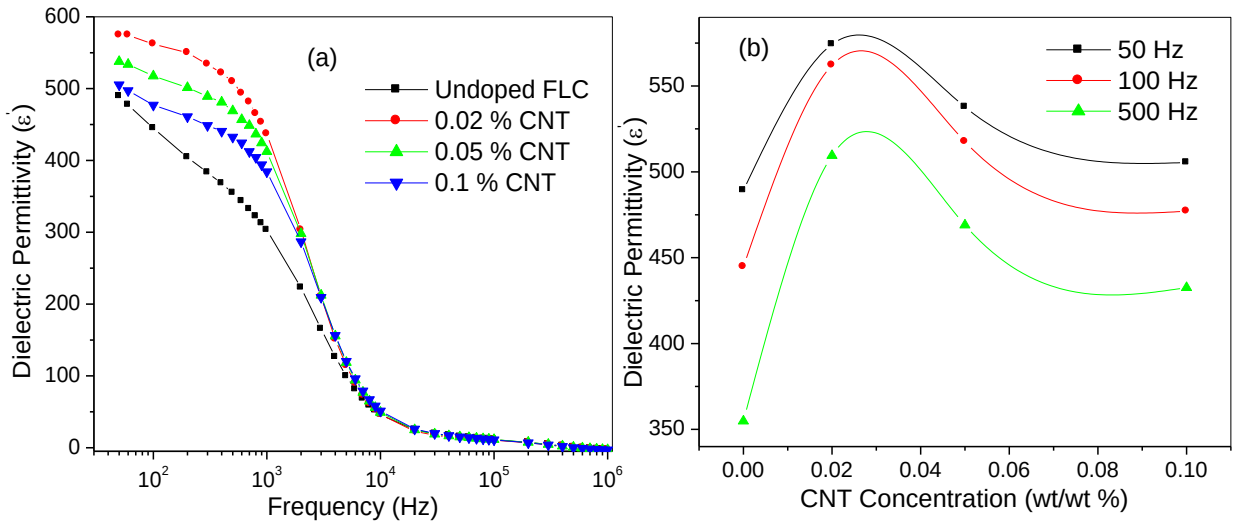


Figure 5.8 Variation in the dielectric permittivity of various samples as a function of (a) frequency and (b) CNT concentration in FLCII matrix ($\Delta T = -5^\circ\text{C}$).

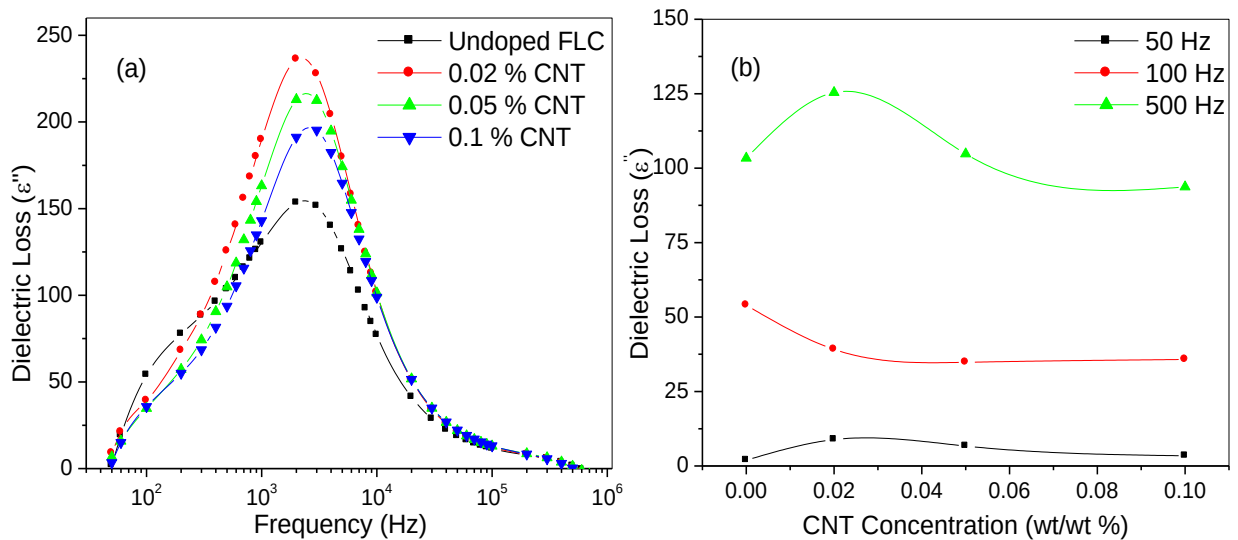


Figure 5.9 Variation in the dielectric loss as a function of (a) frequency and (b) CNT concentration ($\Delta T = -5^\circ\text{C}$).

The variation of dielectric loss as a function of frequency in various CNT-FLCII composites is shown in fig. 5.9(a). It was seen that dielectric loss increases by about 54%, 39% and 25% respectively for 0.02%, 0.05% and 0.1% CNT-FLCII composites over the undoped FLCII at 2 kHz frequency. The low frequencies loss peak (~2 kHz) is due to GM contribution which decreases at higher CNT concentration. It is due to hindrance in the helix unwinding process at higher doping concentration.

Variation in the dielectric loss as a function of CNT concentration is shown in fig. 5.9(b).

AC conductivity

The second loss peak (200 kHz) in fig.5.9 (a) could be due to surface effects which results due to strong anchorage behaviour with substrate surfaces (i.e. conductivity effect due to ITO) and conductivity anisotropy and are connected by

$$\sigma_{AC} = \epsilon_0 \epsilon'' \omega \quad (5.2)$$

where $\omega = 2\pi f$ and ϵ_0 is the permittivity of free space. The variation of ac conductivity as function of frequency and CNT concentration can be observed in fig.5.10 (a, b). At 1 kHz frequency, σ_{AC} for 0.02% CNT-FLCII composite is approximately 46% higher than the undoped FLCII and decreases as the CNT concentration increases to 0.1%.

We also observed sparking in CNT dispersed sample cells when an electric field was applied during the experiments.

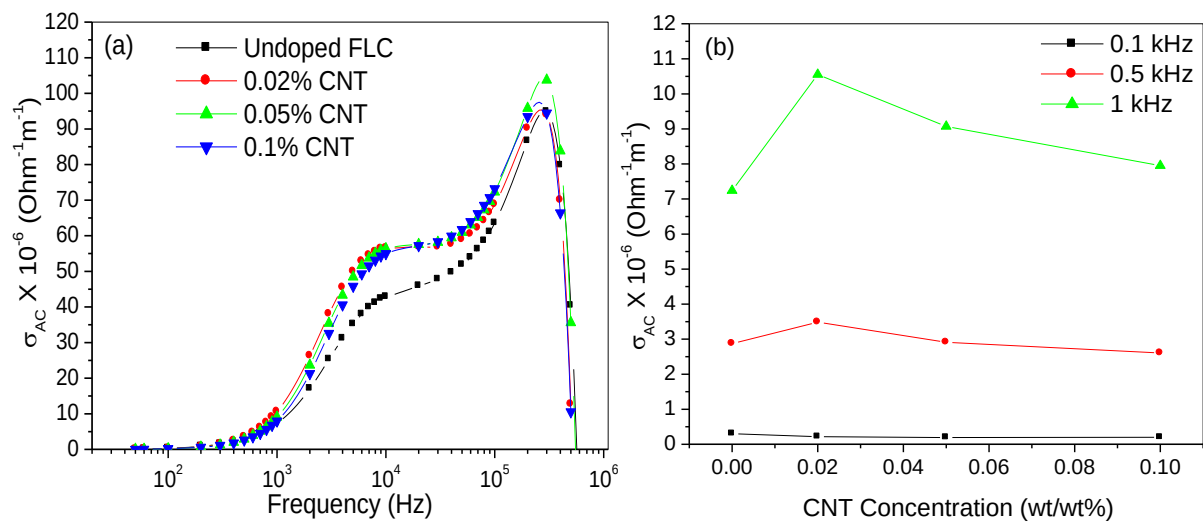


Figure 5.10 Variation of ac conductivity with frequency and with CNT concentration at fixed temperature (-5°C).

Cole-Cole plot and dielectric strength

The dielectric relaxation behavior of various samples in the form of Cole-Cole plot in SmC* phase at -5°C reduced temperature is shown in the fig.5.11 (a). It represents two dielectric relaxations i.e. GM and ITO surface mode (inset). The contribution of LC modes at higher frequencies was likely disturbed by ITO mode and hence neglected.

Fig. 5.11(a) depicts that the contribution of GM is enhanced with CNT addition. However, it is highest for 0.02% CNT-FLCII composite and decreases with increase in CNT concentration.

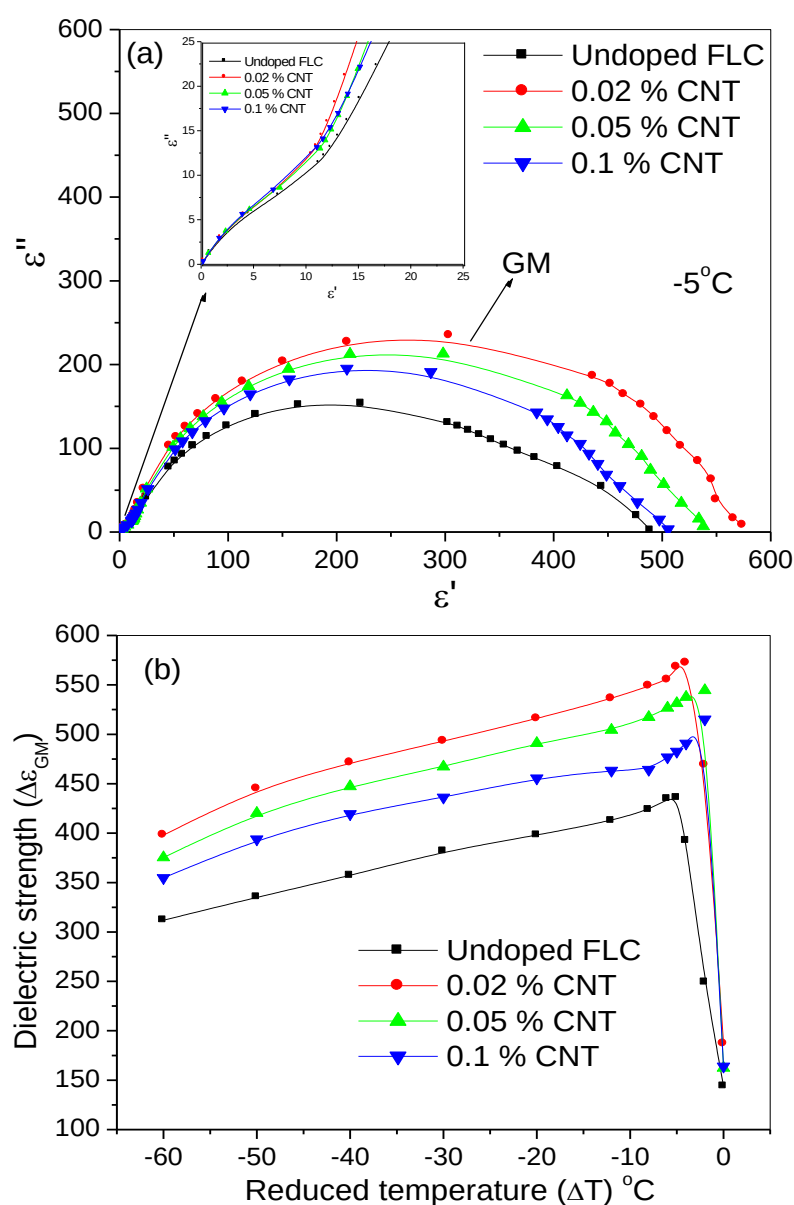


Figure 5.11 (a) Cole-Cole plots in SmC* phase and (b) variation of GM strength with reduced temperature in CNT doped samples.

From the simultaneous fitting of the Cole-Cole plots at various temperatures, dielectric strength ($\Delta\epsilon$) has been calculated and was plotted against reduced temperature as shown in fig.5.11 (b). Dielectric strength increases with CNT addition as compared to undoped FLCII. For 0.02% CNT-FLCII composite, $\Delta\epsilon$ is 14 % higher than the undoped FLCII. But, however, with the increase in CNT concentration, $\Delta\epsilon$ decreases in SmC* phase, thereby showing that the prominent GM contributions are being suppressed by the increasing CNT concentration.

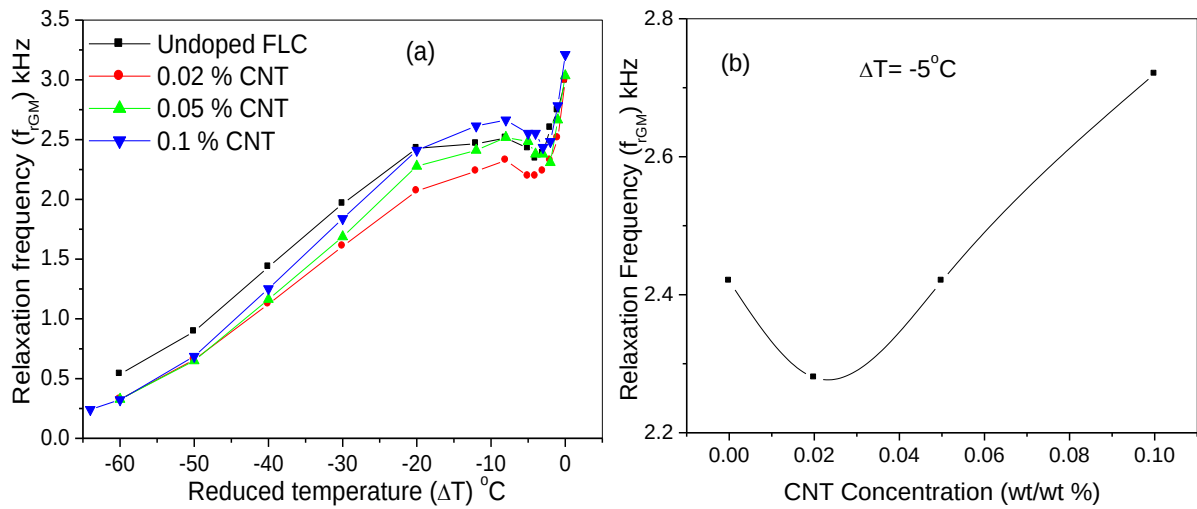


Figure 5.12 Variation of GM relaxation frequencies (a) with reduced temperature in various samples and (b) as a function of CNT concentration in FLCII matrix.

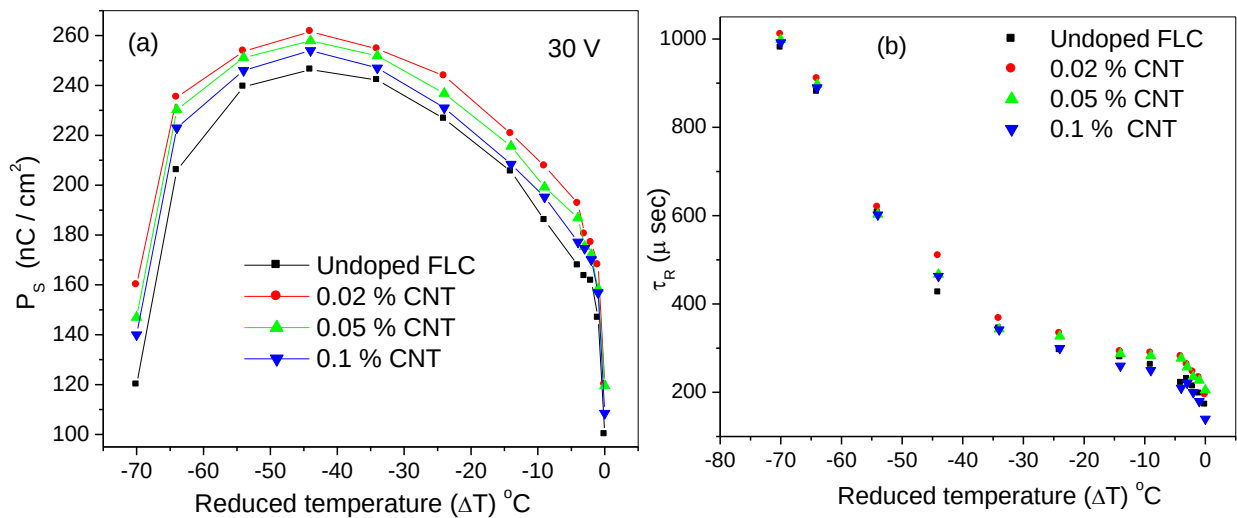


Figure 5.13(a) Variation of spontaneous polarization and (b) response time with reduced temperature in various samples at 30V.

Relaxation frequency

The relaxation frequency of the GM, f_{rGM} as a function of reduced temperature decreases with CNT doping as compared to the undoped FLCII [fig.5.12 (a)]. This may be due to increase in rotational viscosity with the CNT addition.

On the other hand, with increase in CNT concentration f_{rGM} increases and somehow it becomes higher ($\sim 6\%$) for 0.1% CNT-FLCII composite than f_{rGM} of the undoped FLCII in the reduced temperature range from -20°C to 0°C . It means that for this composite, in this temperature region, the molecular motion responsible for the fluctuation of the azimuthal angle in SmC* is faster than the other samples.

The variation of relaxation frequency as a function of CNT concentration in FLCII matrix is shown in fig.5.12 (b). It is clearly reflected that f_{rGM} decreases up to 0.02% but increases thereafter. This increase may be due to increase in the rotational viscosity of the composite over pure material [30].

5.3.4 Electro-optic studies

Spontaneous polarization and response time

The spontaneous polarization (P_s) and response time (τ_R) of the CNT-FLCII composites of different CNT concentrations were calculated and plotted against the reduced temperature as shown in fig.5.13(a, b). The temperature dependence of P_s follows the power law given by eqn.4.7 (chapter 4).

Fig. 5.13(a) shows that P_s decreases with increase in temperature till the transition temperature with and without doping. We noticed about 7% increase in P_s after doping 0.02% CNT in the sample in SmC* phase. As the CNT concentration further increases, the polarization decreases partially but it is still higher than the pure FLCII. This partial decrease could be due to the aggregation of higher concentration of CNTs within the LC matrix. This may align the FLC molecules in the direction of the electric field due to anisotropic interactions and hence decreases the dipole moment.

Response time variation with reduced temperature [fig.5.13 (b)] predicts the increase in τ_R with CNT addition which decreases as the CNT concentration increases. However, for 0.1% CNT sample 7% fast switching in the reduced temperature range from -20°C to 0°C was observed which is also supported by relaxation frequency variations.

REFERENCE

- 1) S. Iijima, Nature **354**, 56 (1991).
- 2) I. Dierking, G. Scalia, P. Morales and D. LeClere, Adv. Mater. **16**, 865 (2004).
- 3) I. Dierking, G. Scalia and P. Morales, J. Appl. Phys. **97**, 044309 (2005).
- 4) I. Dierking and S. E. San, Appl. Phys. Lett., **87**, 83 (2005).
- 5) Michael D. Lynch and David L. Patrick, Nano Letters **2**, 1197 (2002).
- 6) Wei Lee and Hsu-Chih Chen, J. Phys. D. Appl. Phys. **35**, 2260 (2002).
- 7) Wei Lee, Chun-Yu Wang and Yu-Cheng Shih, Appl. Phys. Lett. **85**, 513 (2004).
- 8) In-Su Baik, Sang Youn Jeon and Seung Hee Lee, Appl. Phys. Lett. **87**, 263110 (2005).
- 9) I. Dierking, G. Scalia and P. Morales, J. Appl. Phys. **97**, 044309 (2005).
- 10) I. Dierking and S. Eren San, Appl. Phys. Lett. **87**, 233507 (2005).
- 11) W. Lee, J.S Gau and H.-Y. Chen, Appl. Phys. B **81**, 171 (2005).
- 12) Chei- Yen Huang, Chao-Yuan Hu, Hung-Chih Pan and Kuang-Yao Lo, Jap. J. Appl. Phys. **44**, 8077 (2005).
- 13) Hui-Yu Chin and Wei Lee, Appl. Phys. Lett. **88**, 222105 (2006).
- 14) Sang Youn Jeon, Seung Hwan Shin, Seok Jin Jeong, and Seung Hee Lee, Seok Ho Jeong and Young Hee Lee, Hyun Chul Choi and Kyeong Jin Kim, Appl. Phys. Lett. **90**, 121901 (2007).
- 15) Sang Youn Jeon, Kyung Ah Park, In-Su Bai, Seok Jin Jeong, Seok Ho Jeong, Kay Hyeok An, Seung Hee Lee, and Young Hee Lee, Nano: Brief Reports and Reviews **2**, 41 (2007).
- 16) Seok Jin Jeong, Kyung Ah Park, Seok Ho Jeong, Hee Jin Jeong, Kay Hyeok An, Chang Woon Nah, Didier Pribat, Seung Hee Lee, and Young Hee Lee, Sr., Nano Letters **7**, 2178 (2007).
- 17) A.K. Srivastava, Seok Jin Jeong, Myong-Hoon Lee and Seong Hee Lee, **102**, 043503 (2007).
- 18) L. Lyesetskiy, V. Panikarskaya, O. Sidletskiy, N. Kasian, S. Kositsyn, P. Shtifanyuk, N. Lebovka, M. Lisunova and O. Melezhyk, Mol. Cryst. Liq. Cryst. **478**, 883 (2007).
- 19) Chi-Yen Huang, Ying-Ging Lin and Yi-Jen Huang, Japanese Journal of Applied Physics, **47**, 6407 (2008).

- 20) L. Dolgov, O Yaoshchuk and M. Lebovka, *Mol. Cryst. Liq. Cryst.* **496**, 212 (2008).
- 21) Shin- Ying and Liang-Chy Chien, *Optics Express* **16**, 12777 (2008).
- 22) Ingo Dierking, Katharine Casson and Richard Hampson, *Japanese Journal of Applied Physics*, **47**, 6390 (2008) .
- 23) Jy-Shan Hsu, Wei-Ju Chang, Chao Yu Hu and Hou-Che Li, *Japanese Journal of Applied Physics* **48**, 020220 (2009).
- 24) L.N. Lisetski, S.S. Minenko, A.P. Fedoryako and N.I. Lebovka, *Physica E* **41**, 431 (2009).
- 25) A I Goncharuk, N I Lebovka, L N Lisetski and S S Minenko, *J. Phys. D: Appl. Phys.* **42**, 165411 (2009).
- 26) J. Lagerwall, G. Scalia, M. Haluska, U. Dettlaff-Weglikowska, S.Roth, F. Giesselmann, *Advanced Materials* **19**, 359 (2007).
- 27) V. Weiss, R. Thiruvengadathan and O. Regev, *Langmuir*, **22**, 854 (2006).
- 28) Jan Lagerwall, Giusy Scalia, Miroslav Haluska, Ursula Dettlaff-Weglikowska, Siegmur Roth and Frank Gieselmann, *Adv. Mater.* **19**, 359 (2007).
- 29) P. Malik, A. Chaudhary and K.K. Raina, *Asian Journal of Chemistry* **21**, S095-098 (2009).
- 30) P.Arora, A. Mikulko, F. Podgornov and W. Hasse, *Mol. Cryst. Liq. Cryst.* **502**, 1 (2009).
- 31) Fedor V. Podgornov, Anastasia M. Suvorova, Artsiom V. Lapanik and Wolfgang Haase, *Chemical Physics Letters* **479**, 206 (2009).
- 32) J. Prakash, A. Choudhary, D.S. Mehta and A.M. Biradar, *Physical Review E* **80** 012701 (2009).
- 33) Ravi K Shukla , K K Raina , V Hamplová, M. Kašpar and A. Bubnov, *Phase Transitions* (2011).
- 34) Carbon nanotube from Wikipedia/ the free encyclopedia.
- 35) Carbon Nanotube Science, P. J. F. Harris, Cambridge University Press, 2009.
- 36) C. Dekker, *Physics Today*, 22 (May1999).
- 37) Nanotube images from [www. images.yourdictionary.com/nanotube](http://www.images.yourdictionary.com/nanotube).
- 38) C. Shen, A. Brozena, Y. H. Wang, *Nanoscale* **3**, 503 (2011).

- 39) Jean-Marc Bonard, Frederic Maier, Thomas Stockli, Andre Chatelain, Walt A. de Heer, Jean-Paul Salvetat, Laszlo Forro, Ultramicroscopy **73**, 7 (1998).
- 40) Quanshui Zheng and Qing Jiang, Phys. Rev. Lett. **88**, 045503-1(2002).
- 41) Jun Li, Ramsey Stevens, Lance Delzeit, Hou Tee Ng, Alan Cassell, Jie Han and M. Meyyappan, Appl. Phys. Lett., **81**, 910 (2002).
- 42) Jang Jyongsik, Bae Joonwon and Yoon Seong-Ho, J Mater Chem. **13**, 676 (2003).

CHAPTER 6

Nickel Nanoparticles

Dispersed

Ferroelectric Liquid

Crystal Composites

Overview

In the present chapter, we have made an effort to synthesize nickel nanoparticles by chemical reduction method of a nickel salt. The characterization of these nanoparticles was performed using X-ray diffraction technique and high resolution transmission electron microscopy. The influence of nickel nano particles on the various thermal and electrical parameters (transition temperature, transmission, switching response, permittivity etc.) of a novel room temperature FLC mixture has been studied. The present chapter describes that interaction between nickel nano particles and FLC molecules is due to their respective dipole moments coupling in the presence of applied field. An increase in spontaneous polarization and faster response time has been noticed with nickel addition.

6.1 INTRODUCTION

Continuous efforts are being made to study the consequences of various fillers into the LC matrix, like polymers, dyes, aerosols, CNTs, nanoparticles etc. [1-5]. Since majority of the display industries use nematic systems, nanoparticles dispersed nematic LCs have been extensively studied to further boost the technology [5-7]. However, dispersing nanomaterials into FLCs has been the most developing and promising area since the last few years [8-11]. Research into the practical applications of nano-LC composites has been increasing as they provide promising new materials offering innovative functions. Since nano material densities are much larger than LCs, it is very important to form well dispersed nano-FLC composites and to control the interface between them.

Dispersion of different metallic nanoparticles like gold, platinum and palladium has been reported into various nematic systems [12-18]. According to our literature survey, however, only gold nanoparticles dispersion into FLCs has been reported so far [19-26]. Kumar et al. reported photoluminescence phenomenon in a deformed helix FLC due to presence of optically active phenyl pyrimidine compound which is an electroluminescent material. Also since gold nanoparticles have strong interaction with the visible light, there is an increase in the photoluminescence after their dispersion [19-21]. A number of researchers have shown enhanced dielectric and electro-optic responses in gold nano particles dispersed FLC systems [20-21]. The dielectric response of materials provides information about the orientational adjustment of dipoles and the translational adjustment of mobile charges present in a dielectric medium in response to an applied electric field.

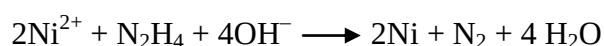
Dielectric spectroscopy of ferroelectrics and related materials enables the independent determination of dielectric permittivity and loss in the dispersion region, as well as the parameters of the various modes related to phase transitions. Besides scientific purposes, dielectric measurements are of increasing importance in display related applications. The electro-optic properties are also of crucial importance. Dielectric and electro-optic parameters fully characterize the manner in which electromagnetic waves propagate within the medium. The difficulties of making measurements on a wide range of materials over a wide frequency (and temperature) range have led to the development of various direct and indirect methods.

The use of nano materials in LCs provides new opportunities and challenges to modify material properties and enhance application range. In this chapter, we report the synthesis of nickel (Ni) nano particles via chemical reduction and studied the influence of these nanoparticles on the various thermal and electrical parameters (transition temperature, transmission, switching response, permittivity etc.) of a novel room temperature FLC mixture. A theoretical approach is given to understand the interaction between Ni nanoparticles and FLC molecules.

6.2 EXPERIMENTAL

Synthesis of nickel nanoparticles

To prepare the Ni nanoparticles, chemical reduction method of nickel salt (NiCl_2) by strong reducing agent (hydrazine hydrate) in the aqueous solution was being used due to better structural control on the microscopic level and low reaction temperature. The molar ratio of $\text{N}_2\text{H}_4/\text{Ni}^{2+}$ poured was 4.5 whereas that of $\text{NaOH}/\text{Ni}^{2+}$ was 2.66. An appropriate amount of hydrazine hydrate (N_2H_4) was taken into a flask of 250 ml and a well shaken solution of NiCl_2 and de-ionized water (taken into burette) was poured drop wise into it at 60°C in 30 minutes. The pink/violet solution thus obtained was stirred for 2 hours. An appropriate amount of NaOH was poured at corresponding reaction temperature and stirred again for an hour. The reduction reaction that takes place can be expressed by the following equation



Due to reduction reaction, the pink/violet solution turned black in 10-15 minutes. The resulting black coloured slurry was washed with de-ionized water repeatedly and filtered

nano powder was dried in the oven overnight at 80°C. The preparation of nickel nanoparticles is also shown in fig. 6.1 in the form of a flow chart.

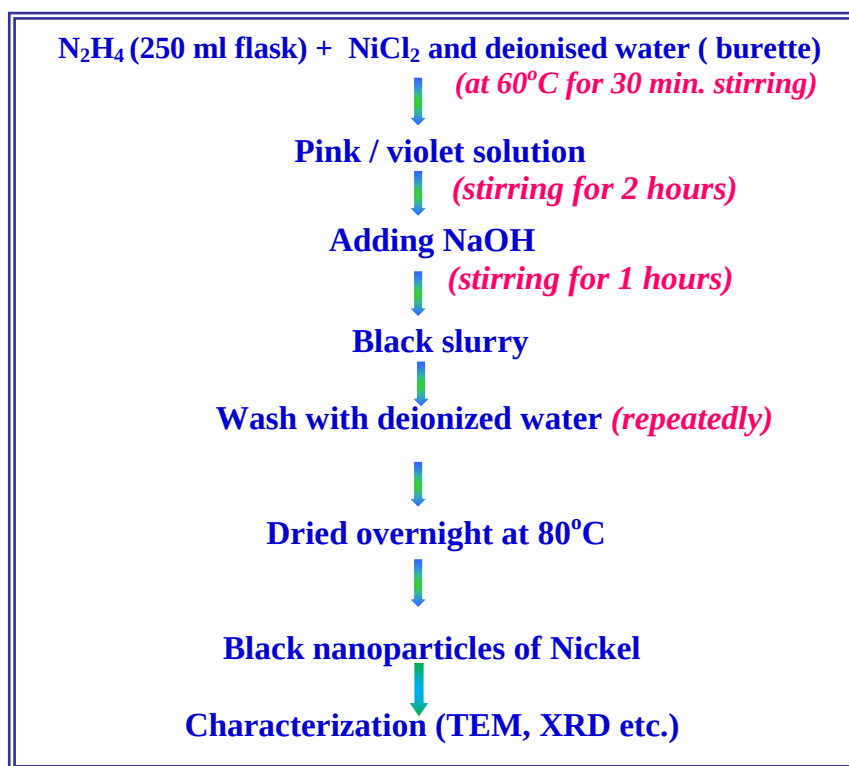


Figure 6.1 Flow chart for the preparation of nickel nanoparticles.

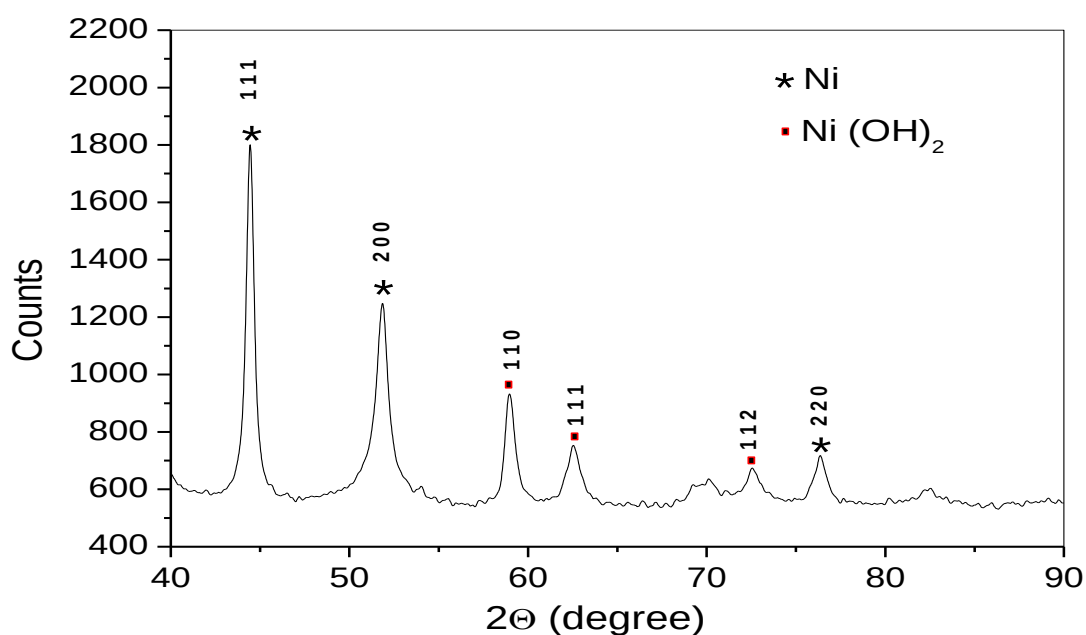
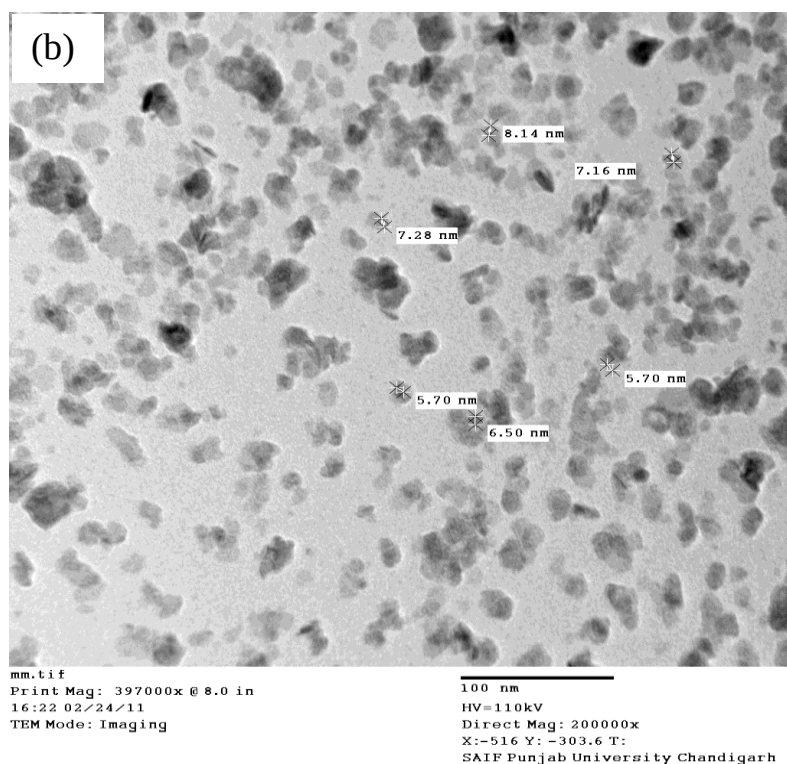
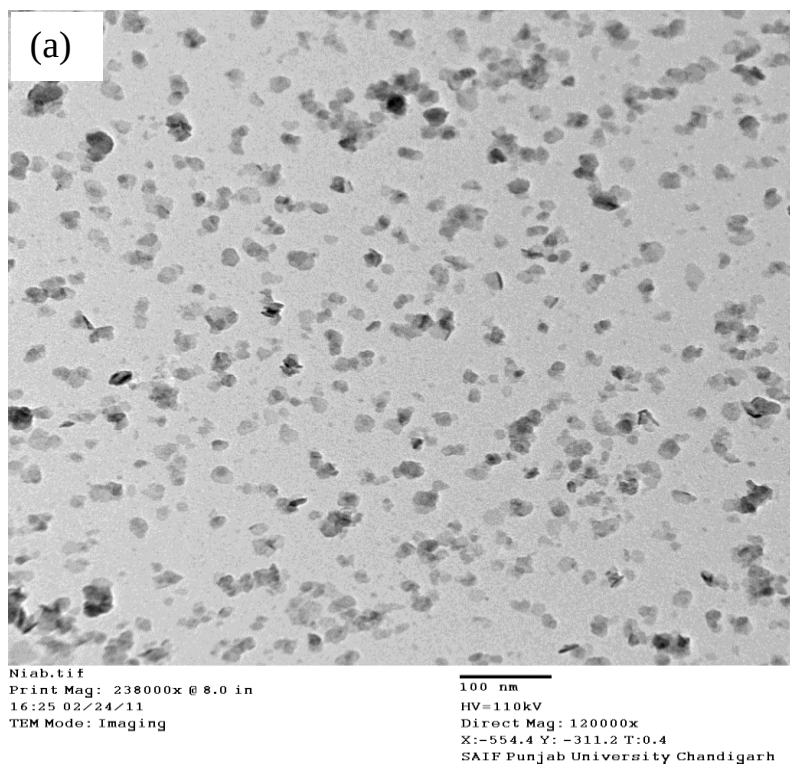


Figure 6.2 XRD pattern of nickel nano powder.



Contd...

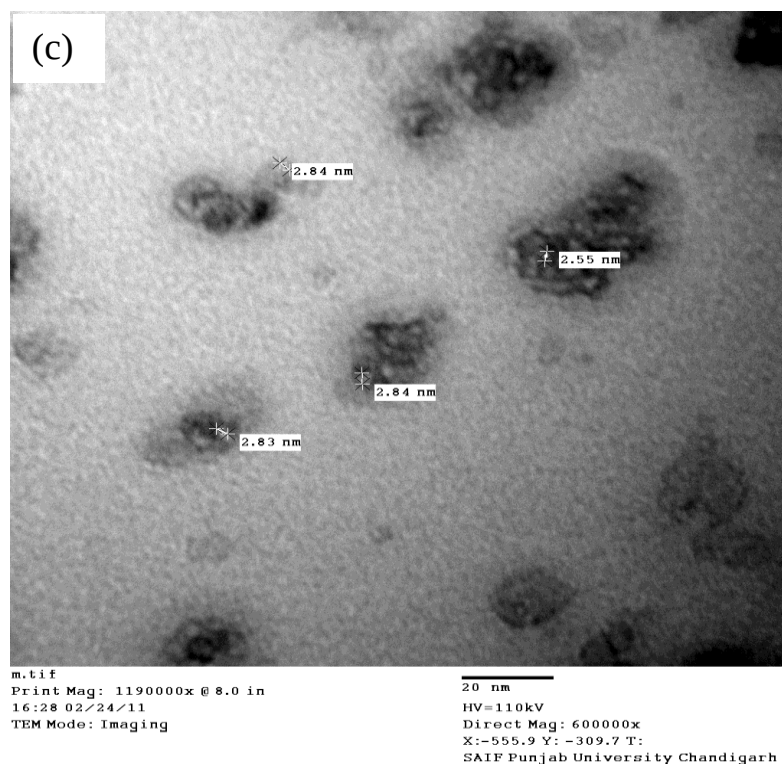


Figure 6.3 TEM micrographs at (a) 120000X (b) 200000X and (c) 600000X magnifications show that particle size of nickel nanoparticles lies between 2-8nm.

6.3 RESULTS AND DISCUSSION

6.3.1 Characterization of nickel nanoparticles

The synthesized Ni nanoparticles were characterized by means of 'XPert PAN analytical' X-ray diffraction (XRD) machine and a HITACHI made transmission electron microscope (TEM) model H7500. The obtained XRD graph (fig.6.2) depicts the formation of two phases i.e. face centered cubic (FCC) phase of Ni metal and hexagonal phase of Ni (OH)₂. However, volume fraction of Ni metal is more as compared to Ni(OH)₂. The TEM studies (fig.6.3) illustrate the spherical shape of nanoparticles whose diameter lies between ~2-8 nm. TEM is a powerful tool for probing the structure and capable of providing morphological information.

6.3.2 Transition temperature changes

We also studied the effect of Ni nanoparticles on the transition temperature of various phases of FLCIII using thermal optical polarizing microscopy. An increase of about 2°C was observed in isotropic temperature (Table 6.1) of 0.5% Ni-FLCIII composite which

suggests the possibility of strong interactions between Ni nanoparticles and FLC molecules since metals have large stiffness and better interfacial bonding.

Table 6.1: Transition temperature of different phases

Samples	SmC*-SmA	SmA-N*	N*-Iso
Undoped FLC III	62.0	76.0	86.0
FLC III + 0.5 wt% Ni	63.7	77.4	87.2

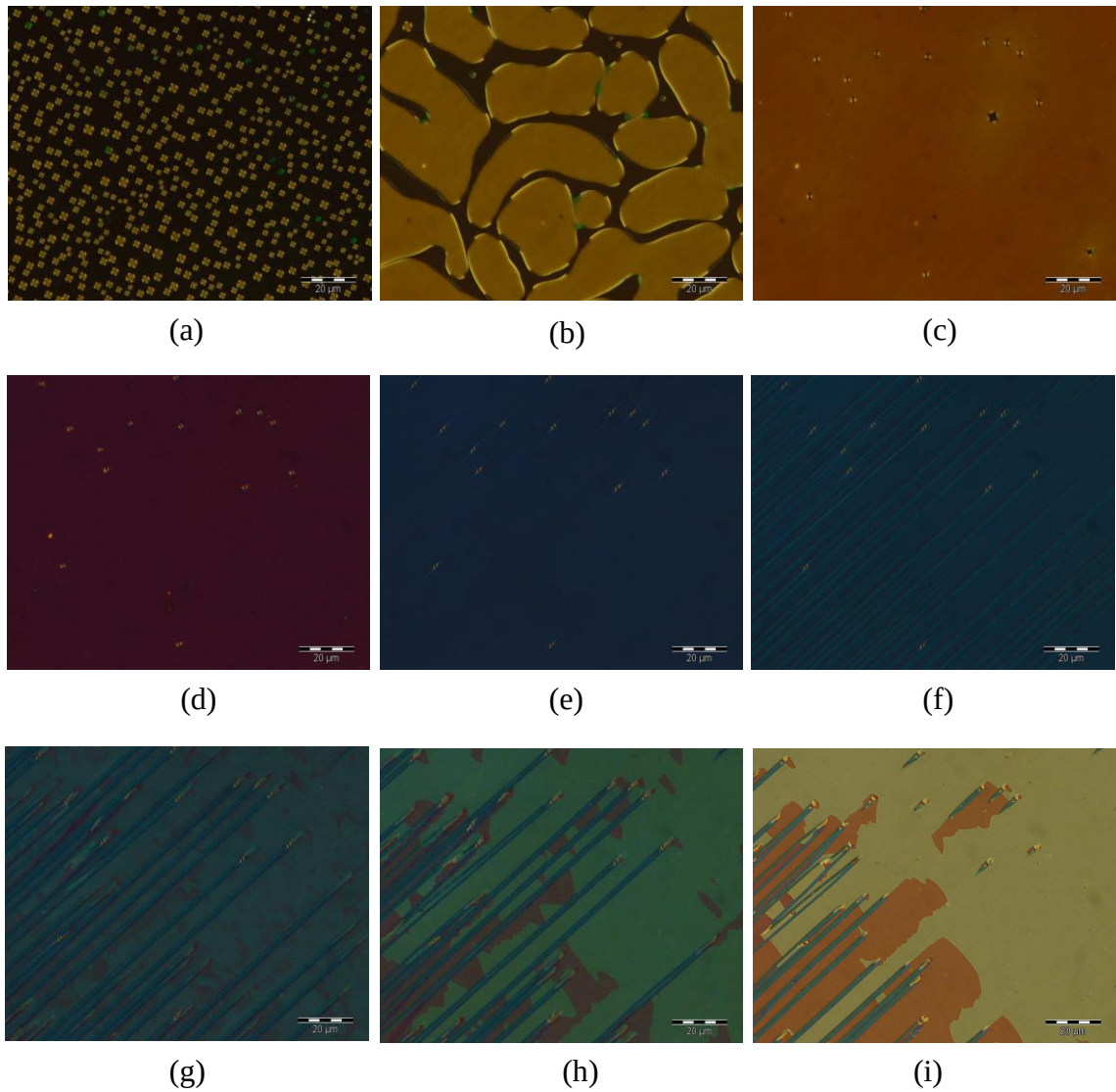


Figure 6.4 Optical textures of 0.5% Ni-FLCIII composite at (a) 87°C (b) 85°C (c) 80°C (d) 75°C (e) 66 °C (f) 65°C (g) 60°C (h) 55°C (i) 30°C respectively.

6.3.3 Textural studies

To get insights into the internal structure of Ni-FLCIII composite, we have studied the optical micrographs under cross polarizers. Fig. 6.4 shows the sequence of microtextures obtained upon cooling the 0.5% Ni-FLCIII composite from isotropic temperature.

We observed that zig-zag defects were reduced in the Ni-FLCIII composite as compared to undoped FLCIII as shown in fig.6.5(a, c). This suggests that addition of Ni nanoparticles has minimized the defects and hence improved the optical transmission. Although Ni nanoparticles are ferromagnetic in nature but FLC matrix does not offer any contribution towards the magnetic properties. We apply the magnetic field of 0.1tesla to the Ni-FLCIII composite but did not find any textural changes in the composite. Also it can be depicted from fig.6.5 (b, d) that number of light leakage centers has been increased in Ni-FLCIII composite [27].

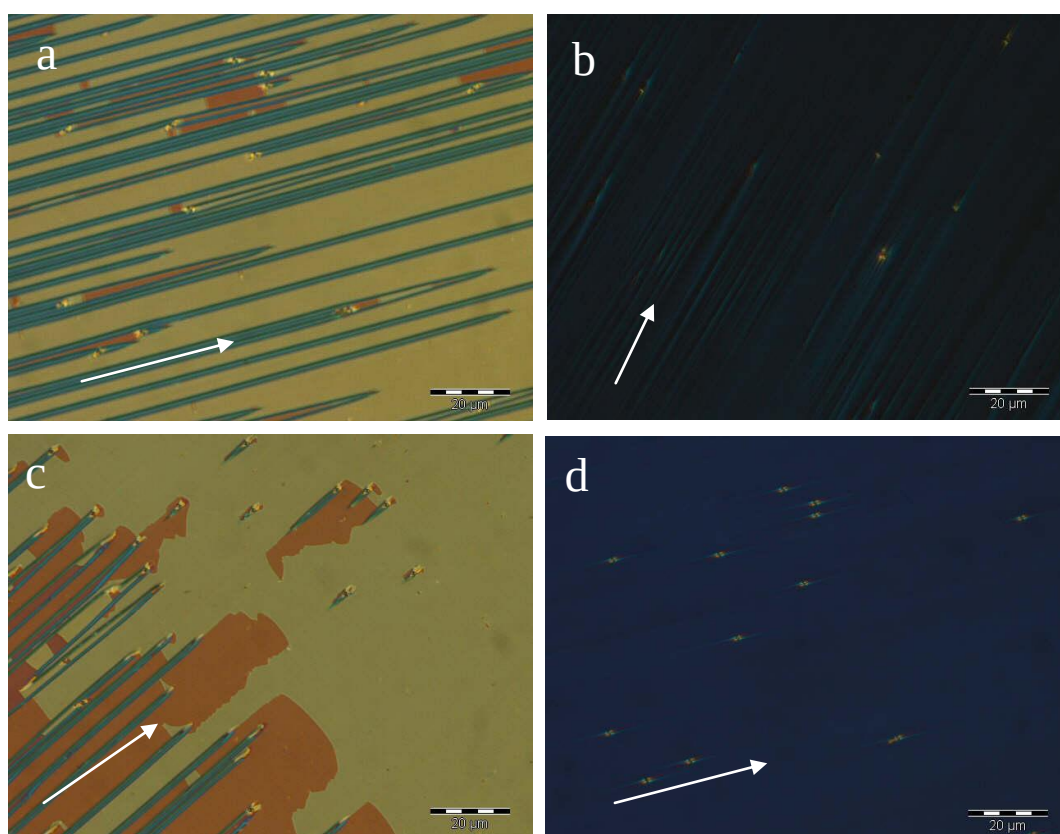


Figure 6.5 Optical micrographs of (a) SmC* (b) SmA phases of undoped FLCIII and (c) SmC* (d) SmA phases of 0.5% Ni-FLCIII composite. Arrows show the rubbing direction.

6.3.4 Electro-optic studies

Fig.6.6 (a) shows the optical behaviour of undoped and doped FLCIII material to an incident light. The optical transmission through the sample can be computed by Beer's law

$$T = \frac{I_t}{I_o} = e^{-(\alpha+\beta)d} \quad (6.1)$$

where I_o , I_t are the incident and transmitted light intensity, d is sample thickness, α and β reflect scattering and absorption coefficients of the film respectively. α is a function of material properties [28].

We measured the optical behaviour of undoped FLCIII and Ni-FLCIII composite at room temperature using UV-VIS spectrophotometer (Analytik Jena's Specord 205) in the wavelength range of 200-800nm. The output responses were obtained on the computer interfaced to the spectrophotometer.

In our case, unlike dye doped LCs [28], neither undoped FLCIII nor Ni-FLCIII composite show any absorption in the visible region (400-780 nm) as shown in fig.6.6 (b). Since scattering is negligible in thin films, it implies that there will be maximum transmission of the incident light. These factors deny any possibility of excitation of Ni nanoparticles by visible light as reported earlier for gold nanoparticles [20-21]. Thus, increase in transmission is entirely due to ordering of FLC molecules by Ni nanoparticles.

It is also confirmed by variation of the tilt angle which is one of the fundamental order parameters of FLCs. An increase in the tilt angle has been depicted in Ni-FLCIII composite over undoped FLCIII as shown in fig.6.6(c) that may be due to ordering of FLC molecules by Ni nanoparticles.

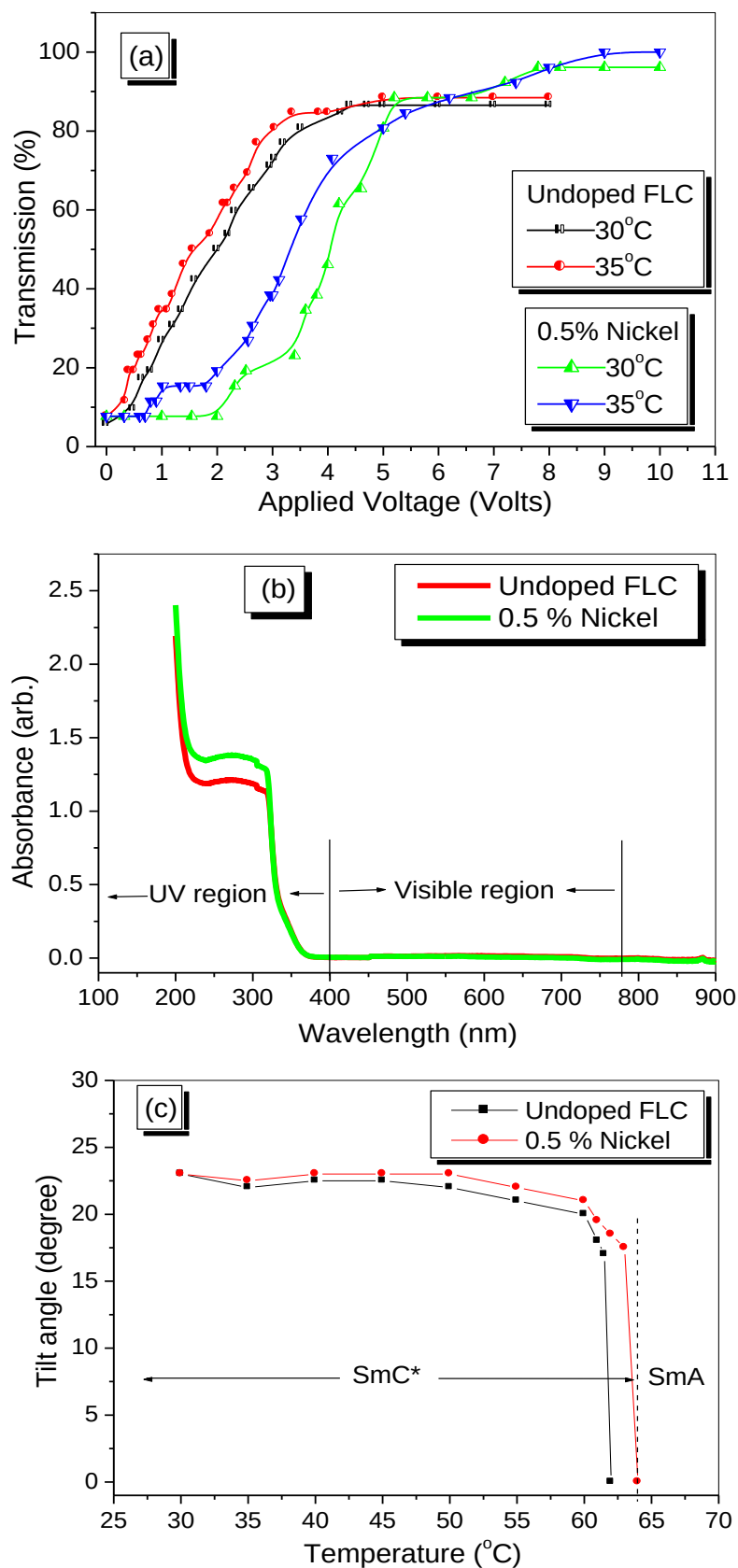


Figure 6.6 (a) Optical transmission as a function of applied voltage at fixed frequency 50Hz (b) UV-Vis graph and (c) tilt angle variation with temperature in the two samples.

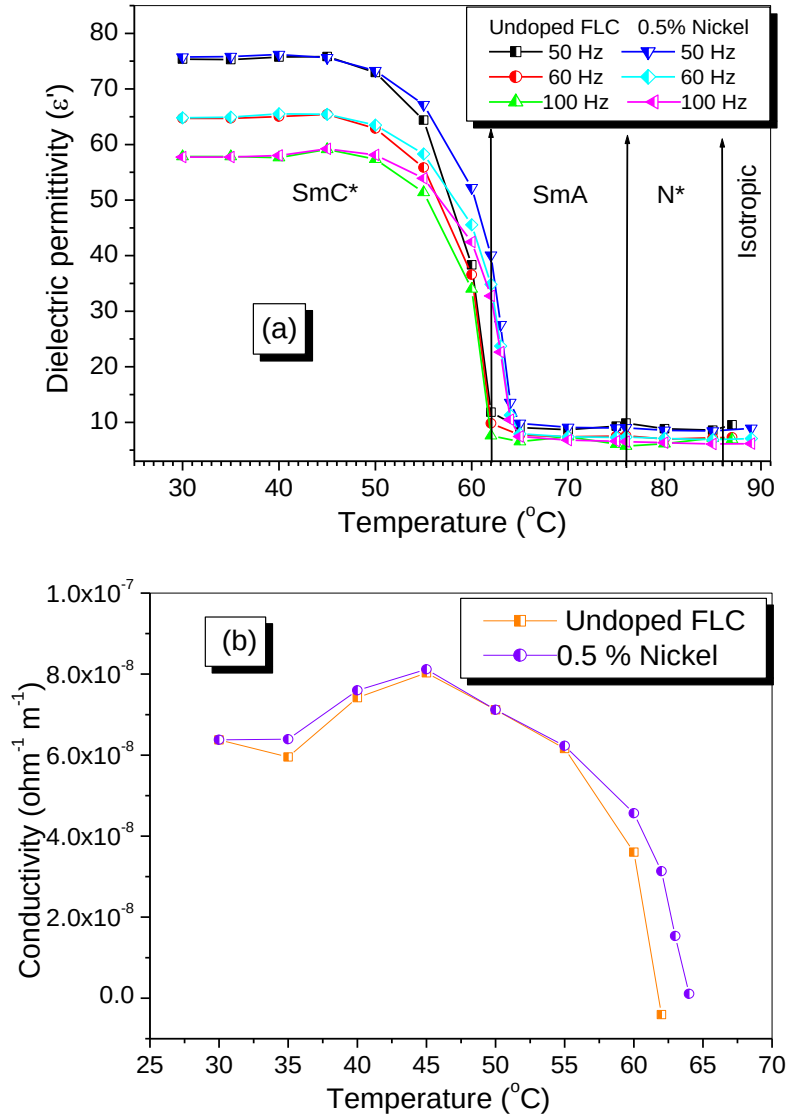


Figure 6.7 Temperature variations of (a) dielectric permittivity at different frequencies and (b) conductivity at 100Hz frequency.

6.3.5 Opto-dielectric responses

The variation of real part of relative dielectric permittivity of FLCIII and Ni-FLCIII composite is depicted in fig.6.7 (a). The ϵ' was found to increase by 1% to 26% with nickel addition especially near SmC*-SmA phase transition. This phenomenon of increase in ϵ' with Ni addition can be attributed to the enhancement of electrical conductivity of the composite due to incorporation of metal particles (nickel) as filler. An increase in the conductivity of Ni-FLCIII composite as a function of temperature can be noticed in fig. 6.7(b).

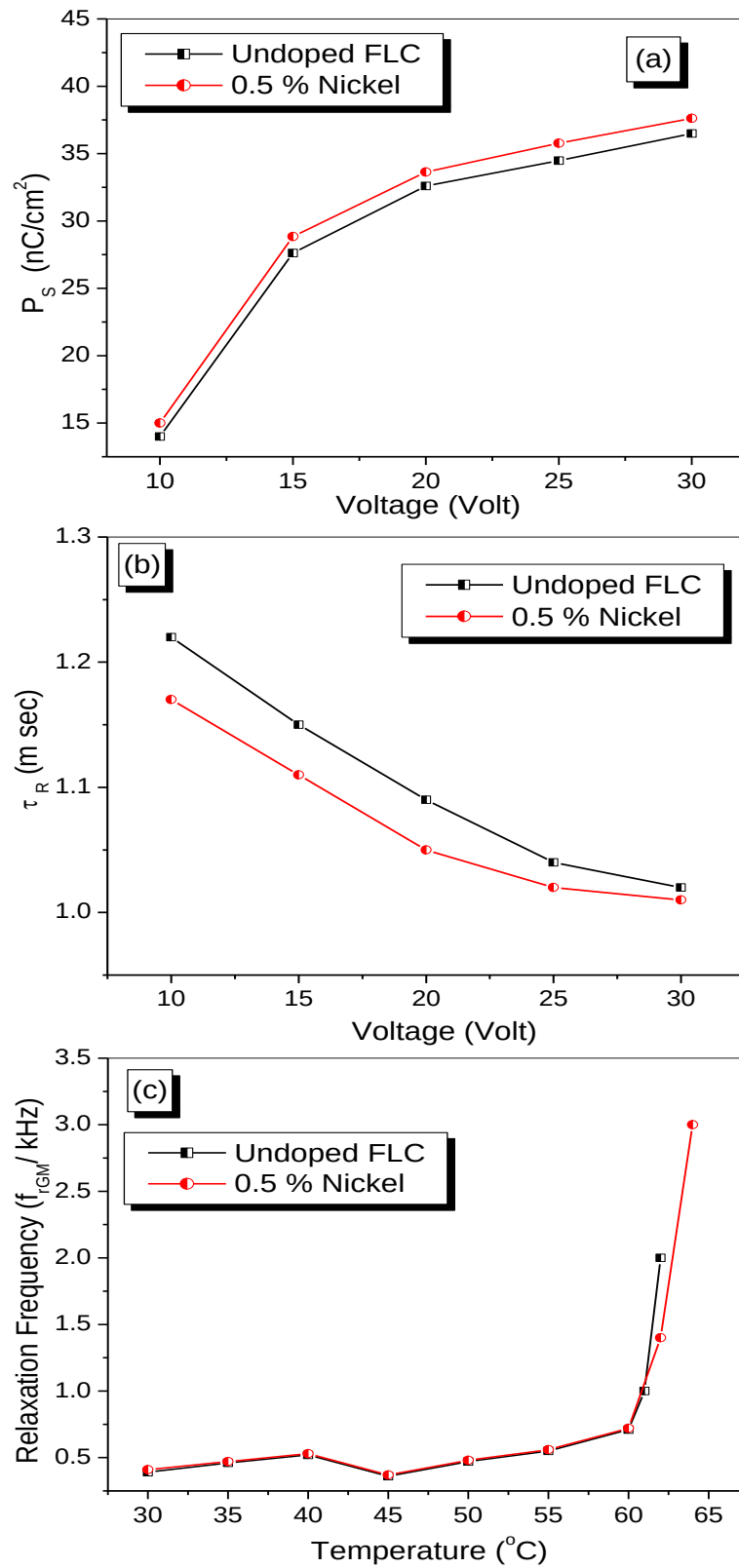


Figure 6.8 Variation of (a) spontaneous polarization and (b) response time as a function of applied voltage at room temperature (30°C) (c) relaxation frequency as a function of temperature.

FLC matrix is made of polar molecules which undergo orientational polarization and can give rise to the enhanced polarization as compared to undoped FLCIII and this explains its higher dielectric permittivity. Also nano structured materials possess dielectric behavior due to different types of polarizations present in the material. Interfaces present in them give dipole moment which orient in the presence of electric field along its direction (dipole moment for Ni is $\sim > 10\text{D}$ and LC molecules is $\sim 2\text{D}$). Thus high value of dielectric constant at low frequencies is due to space charge polarization and rotation direction polarization. Increase in temperature will increase the dipole moment. This is why dielectric constant of composite material is enhanced near SmC^* - SmA transition temperature.

6.3.6 Switching responses

Fig. 6.8 (a) shows the variation of spontaneous polarization P_s , response time τ_R and relaxation frequency f_r in the two samples. Fig. 6.8 (b) depicts that P_s is higher for Ni-FLCIII composite as compared to undoped FLCIII which is the consequence of increase in the net dipole moment in the presence of electric field in its direction. A faster response time has been noticed with Ni addition. The response time is inversely related to the relaxation frequency by the following relation

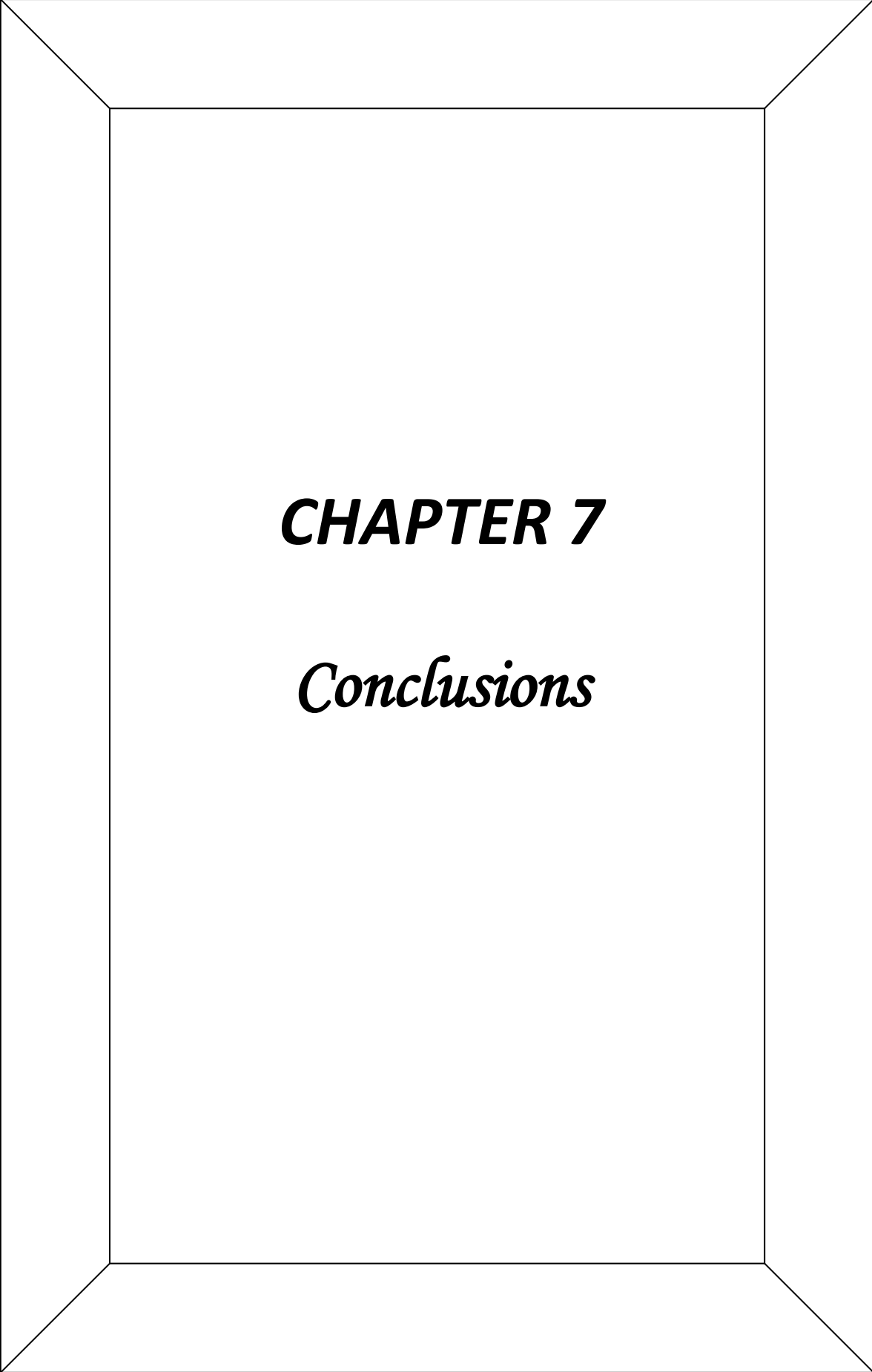
$$\tau_R = \frac{1}{2\pi f_r} \quad (6.2)$$

As f_r increases in Ni-FLCIII composite [fig.6.8 (c)], a decrease in the response time has been resulted. The temperature dependence of f_r shows a sharp increase near the SmC^* to SmA phase transition.

REFERENCES

- 1) Parveen Malik, K.K.Raina and A.K. Gathania, Thin Solid Films, **519**, 1047 (2010).
- 2) Samriti Khosla, Nitin sood, K.K. Raina and S.S. Bawa, Mol. Cryst. Liq. Cryst. **524**, 119 (2010).
- 3) G. Sinha, J. Leys, C. Glorieux and G. Theon, J. Non-Cryst. Solids, **351**, 2780 (2005).
- 4) Hari Krishna Bisoyi and Sandeep Kumar, Chem. Soc. Rev. **40**,306 (2011).
- 5) Wei Lee, Chun-Yu Wang and Yu- Cheng Shih, Appl. Phys. Lett. **85**, 513 (2004).
- 6) Shie-Chang Jeng, Shung-June Hwang and Chen-Yu Yang, Opt. Lett. **34**, 455 (2009).
- 7) Liliana Cseh and George H. Mehl, J. Mat. Chem. **17**, 311 (2007).
- 8) Neeraj and K.K. Raina, Phase Transitions **83**, 615 (2010).
- 9) Neeraj and K. K. Raina, Integrated Ferroelectrics **125**, 104 (2011).
- 10) Liu-Shiaun Li and Jung Y Huang, J Phys D: Appl. Phys., **42**, 125413 (2009).
- 11) A. Kumar, J. Prakash, P. Goel, T. Khan, S. K. Dhawan, P. Silotia and A. M. Biradar, Europhysics Letters **88**, 26003 (2009).
- 12) M. Urbanski, B. Kinkead, H. Qi, T. Hegmann and H.-S. Kitzerov, Nanoscale **2**, 118 (2010).
- 13) N. Nishida, Y. Shiraishi, S. Kobayashi and N. Toshima, J. Phys. Chem. C **112**, 20284 (2008).
- 14) H.Shiraki, S. Kundu, Y. Sakai, T. Masumi, Y. Shiraishi, N. Toshima and S. Kobayashi, Jap. J. Appl. Phys. **43**, 5425 (2004).
- 15) Michel Mitov, Francois de Guerville and Christian Bourgerette, Mol.Cryst. Liq. Cryst. **435**, 13/[673] (2005).
- 16) Yukihide Shiraishi and Naoki Toshima, Appl. Phys. Lett.**81**, 2845 (2002).
- 17) Michel Mitov, Christian Bourgerette and Francois de Guerville, J. Phys.: Condens. Matter **16**, S1981 (2004).
- 18) Liliana Cseh and georg H. Mehl, J. Mater. Chem. **17**, 311 (2007).
- 19) A. Kumar, J. Praksh, D.S. Mehta, A.M. Biradar and W. Haase, Appl. Phys. Lett. **95**, 023117 (2009).
- 20) S. Kaur, S.P. Singh and A.M. Biradar, Appl. Phys. Lett. **91**, 023120 (2007).

- 21) S. K. Prasad, K.L. Sandhya, Geetha G. Nair, Uma S. Hiremath, C.V. Yelamagga and S. Sampath, *Liq. Cryst.* **33**, 1121 (2006).
- 22) Thomas Härtling and Lukas M. Eng, (2005), *Appl. Phys. Lett.* **87**, 142902.
- 23) J. Prakash, A. Choudhary, A. Kumar, D.S. Mehta and A.M. Biradar, *Appl. Phys. Lett.* **93**, 112904 (2008).
- 24) F.V. Podgorov, A. V. Ryzhkova and W. Haase, *Appl. Phys. Lett.* **97**, 212903 (2010).
- 25) S. Sridevi, S. K. Prasad, G. G. Nair, V. D'Britto and B.L.V. Prasad, *Appl. Phys. Lett.* **97**, 151913 (2010).
- 26) T. Joshi, A. Kumar, J. Prakash and A. M. Biradar, *Liq. Cryst.* **37**, 1433 (2010).
- 27) T. Joshi, A. Kumar, J. Prakash and A. M. Biradar, *Appl. Phys. Lett.* **96**, 253109 (2010).
- 28) Jin-Jei Wu, Chih-Ming Wang, Wang-Yang Li and Shu-Hsia Chen, *Jpn. J. Appl. Phys.* **37**, 6434 (1998).



CHAPTER 7

Conclusions

Overview

In this chapter, we have summarized the important features and results obtained from thermal, dielectric and electro-optic studies of nano materials dispersed ferroelectric liquid crystal systems as discussed in chapter 4, 5 and 6. The future possibilities have been explored on the basis of this research work from basic and applied research point of view.

We attempted to understand the dynamic mechanisms of nano dispersed ferroelectric liquid crystal composites after dispersing the SiO₂, MWCNTs and Nickel nano materials respectively into different FLC matrix. The detailed studies were carried out in planer aligned cells to obtain various thermal, dielectric and electro-optic parameters of these composites. We elaborated the dependence of these properties on various factors and made the following conclusions

- ✿ The interaction between nano materials and liquid crystals depends upon many factors, like (a) nature of dispersing materials (b) shape and size of nano materials (c) concentration of nano materials into LC host (d) physical and chemical properties of LCs and nano materials and (e) magnitude of applied electric field parameters.
- ✿ Dispersion of silica nano particles lead to change in structural properties of liquid crystals which may be due to anchoring effects introduced by the anisotropic interactions between silica–LC molecules (fig.4.2). Dielectric properties of FLCI are strongly influenced by silica nanoparticles. At low frequency, dielectric permittivity (ϵ') decreases with an increase in silica concentration in the SmC* phase. Two loss peaks were observed in the frequency range from 50 Hz to 1MHz. Low frequency loss decreases with the increase in silica concentration, but at high frequency, the loss peak shifted towards the higher frequency region (fig. 4.6). The second loss peak is dominated by the characteristic absorption effect of ITO coated substrates.
- ✿ Switching studies depicts that P_s decreases by about 14% [fig. 4.13(b)] in 0.01% silica sample whereas 23% in 0.1% silica sample respectively as compared to undoped mixture at -25°C reduced temperature. τ_R was found to be 22% [fig. 4.15(a)] faster in 0.01% sample as compared to 0.1% sample.

- ✿ The optical transmission was higher (fig. 4.16) in the silica doped FLCI composites than the undoped sample and optical contrast increases 3 times (fig. 4.17) in 0.1% silica sample than undoped FLCI mixture. It may be due to alignment of LC molecules by silica nanoparticles in the direction of applied electric field which results into low scattering state of incident light and hence the transmission increases. Also there is a substantial decrease in the driving voltage after SiO₂ addition. Since driving voltage depends upon numerous factors like cell thickness, anchoring effect etc. so its decrease with increase in silica concentration may be due to the anchoring of FLCI molecules by silica nano particles.
- ✿ The studies on CNT-FLCII composites show that transition temperature increases and is a function of CNT concentration. Decrease in the threshold voltage of switching of molecules was seen in 0.02% CNT-FLCII composite (fig. 5.6). An increase in the dielectric permittivity by 20 to 40 % (fig. 5.8) and dielectric loss by 25 to 54% (fig.5.9) has been observed in CNT dispersed FLCII composites from 50 Hz to 1 kHz frequency range. The conductivity anisotropy and dipolar interaction contribute to this variation.
- ✿ An increase in polarization by 7% [fig. 5.13(a)] was depicted for 0.02% CNT-FLCII composite due to increase in dipole moment and about 7% [fig. 5.13(b)] fast switching was observed for 0.1% CNT-FLCII composite in the reduced temperature range from -20°C to 0°C.
- ✿ The Nickel-FLCIII composite show improved optical transmittance and switching response attributed to the strong interactions. These studies indicate that metallic nanoparticles in LC matrix can provide better opto-electronic behaviour and should pave a new pathway to the advanced nano metal-FLC composite materials in displays.
- ✿ The results of thermo-optic, electro-optic and dielectric characterizations of various nano dispersed ferroelectric liquid crystal composites show that collaboration of liquid crystals and nanotechnology will contribute to the development of new display devices and will help to improve the performance of high contrast displays, spatial light modulators, electro-optic switches, adaptive optics elements etc.