CHAPTER I

INTRODUCTION

1.1 Ferroelectricity in organic materials:

The interesting property due to the reversibility of the spontaneous polarization, which was observed for a long time only amongst the inorganic crystalline solids, now encompasses variety of organic materials. To start with, the first ferroelectric was the amino acid derivative triglycine sulphate (1) in which the glycine, one of the important biological molecules, plays a significant role for the onset of the ferroelectric behaviour. Later on, some more organic ferroelectric substances like Guanidine Aluminium sulphate hexa hydrate (2), thiourea (3), Ammonium Chloroacetate (4), Trisarcosine Calcium chloride (5), Semicarbazide hydrochloride (6) were reported to be ferroelectric. Few recent reports on ferroelastic ferroelectric- Tanane (7) (C$_9$H$_8$S$_5$I) and 2-alkyl-benzimidazole (8) have also appeared in the literature. The interest in the organic ferroelectric materials has been triggered also with a view to find some new classes in which the hydrogen bond may be responsible for the onset of ferroelectricity. In addition to the presence of hydrogen bond it is also necessary that the compound should have two isomers
with identical stability and the transition is obtained by proton switching from one isomer to the other. The search for ferroelectricity in Benzimidazole was with this view; however, on the contrary, Tanane does not contain intermolecular hydrogen bonding. This is an example of pure molecular solid to be ferroelectric without having a hydrogen bond.

The concluding remark is that a hydrogen bond is not always a necessary condition for ferroelectricity, though in the biological materials, the existence of hydrogen bonds will probably always be the most important cause for ferroelectricity (DNA?).

Meanwhile many of the organic and biological materials were reported to show interesting pyroelectric and piezoelectric properties. These studies have drawn the interest of research workers in the field of ferroelectricity to investigate some of these materials (1-11) for their potential ferroelectric behaviour.

Perhaps the conclusion of Von Hippel (12) that a variety of polar coupling phenomena can be expected to produce ferroelectricity and antiferroelectricity in nonliving and also in biological systems and that true relation may exist between ferroelectricity, formation of liquid crystals, and generation of electric impulses in nerves and muscles, was one of the driving forces for the research pursuits in this direction.
Since then essentially it is in the seventies that work on ferroelectric liquid crystal was initiated. The combination of ferroelectricity along with liquid like properties leads to remarkable effects like "flow induced polarization" and makes this new class of ferroelectric materials worthwhile for investigations. The development and the current state of knowledge of ferroelectric liquid crystals in the past five years, have reached an interesting stage, and the original conjectures in this class of materials (13) have been remarkably experimentally confirmed. Synthesis (14) of new molecules (DHBHSC) (Chiral smectic C phase) led to the first experiments on electro-optical properties (15, 16), indicating spontaneous polarization, shear induced polarization (17), pyroelectric effects (18), switching (19), studies on the Curie point and visible effects in freely suspended films (20). Their comparison with crystalline ferroelectrics have been discussed in details (21).

The potential applications of the electro-optical effects (22-26) in the ferroelectric phase of the liquid crystal are being currently explored. More interesting are the possible switching effects in very thin layers between conducting glass plates in which surface pinning effects may be utilized to active electro-optical memory.
Purpose of Study:

As yet only a limited number of ferroelectric liquid crystals in the form of thick films have helped in understanding the unique nature and the limitation of ferroelectric behaviour under certain conditions in this new class of material. The dielectric study through loss and relaxation behaviour, phase transition and spontaneous polarization through their pyroelectric measurements, are likely to throw light on its structural mechanism, for the occurrence of its ferroelectric properties. Hence the effort of this thesis is to extend the investigations of few ferroelectric and related liquid crystals on the enumerated points. The scheme of this study hence follows in reviewing following points relevant to our own objective of this thesis:

(1) The basic aspects of liquid crystals (1.2)
(2) The ferroelectric liquid crystals (1.2.1)
(3) Pyroelectricity in relation to ferroelectrics (1.3)
(4) Pyroelectricity in ferroelectric liquid crystals (1.3.1)
(5) Dielectric study, in general, of organic materials and liquid crystals (1.4)
(6) Dielectric study, in particular, of ferroelectric liquid crystals (1.4.1)
1.2 The liquid crystals

The unusual feature of liquid crystals is that during the melting process, as a first step, which occurs at a definite temperature, the crystal loses its three dimensional state of order and transforms into a two dimensional or one dimensional state of order. The melt which is formed, however, still contains layers of molecules which can be displaced relatively to each other. These molecular aggregates in the form of layers or strands give the melt anisotropic properties usually found only in crystal. For such substances "LIQUID CRYSTAL" name was proposed to describe the intermediate state. Although substances of this class have been known for a long time, they have recently acquired special significance in fundamental research and various practical applications by reasons of their unusual behaviour.

Depending on the relative position of the molecules, the molecular aggregates gives rise to "three" types of mesomorphic phases, which are designated as smectic, nematic and cholesteric mesophases.

The smectic mesophase is a translucent, highly viscous state. The essential features of the structure being that the molecules arranged in layers with their long axis are parallel to each other in the layers and
approximately normal to the plane of the layers. The molecules can move in two directions in the plane and they can rotate about one axis. The spacing of the molecules in each layer is not uniform as it would be in a true crystal. Within the layers which are approximately 20 Å thick, the molecules can be arranged either in neat rows or randomly distributed. In addition, the planes can slide without hindrance over similar neighbouring layers. They are further classified into A B C D E F G and H sub-groups respectively by X-ray analysis (27).

The properties of nematic phase indicate that the molecules are approximately parallel to one another, but they are not in layers. That is, the long axis of the molecule in this structure maintains a parallel arrangement to each other. They are mobile in three directions and can rotate about one axis. It must be concluded that the molecules can be drawn past one another in the direction of their long axis, a degree of freedom which is excluded in smectic phases by the comparatively strong attractions between the ends of the molecules. This agrees with the fact that nematic phase are in general more fluid than smectic phases. The essential difference between them is that smectic phase have a stratified (helical) structure, the molecules being arranged in layers with their long axes approximately normal to the planes of layers,
while in nematic phase the only restriction on the arrangement is that the molecules preserve a parallel orientation.

The cholesteric structure consists of parallel monomolecular layers in which the direction of the long axis of molecules in a chosen layer is slightly displaced from the direction of the axis of molecules in an adjacent layer. This displacement of direction continues from one layer to another resulting in a helical structure. This helical molecular ordering gives rise to a circular dichroism for light propagating parallel to the helical axis.

1.2.1 Ferroelectric liquid crystal:

The fundamental definition of ferroelectricity requires two properties, spontaneous polarization and the ability to reorient the polarization within the crystal with a small external field. The second condition is satisfied in the liquid crystal by the fluid nature of the ordering in the liquid crystal layers, allowing easy reorientation of the molecules in response to an applied field. Beyond the practical satisfaction of the definition, however, the liquid crystalline ferroelectrics are quite different from crystalline ones.

Experiments have shown that permanent dipole order of the ferroelectric type is present in liquid
crystals. The question arises; does such ordering in liquid crystals lead to the emergence of properties specific to classical crystalline ferroelectrics? Though the spontaneous polarization in liquid crystal is only a fraction of a Debye per molecule and thus much smaller than in crystalline ferroelectrics, the combination of ferroelectricity with liquid like properties is certainly intriguing leading to some remarkable effects like flow induced polarization (15).

The important difference between liquid and solid ferroelectrics — first pointed out by Zacharyan (20) — is that there is no anisotropy of the direction of the spontaneous polarization in liquid crystalline ferroelectrics. Another interesting aspect of liquid crystalline ferroelectrics is that, in contrast to solid ferroelectrics, a continuous symmetry group is broken at $T_C$. There are an infinite number of possible domains below $T_C$. Thus the spontaneous polarization will continuously rotate as one goes from one domain to the other and we expect to find a helical cholesteric type structure.

There are essentially two ways in which ferroelectricity may arise in liquid crystals carrying permanent dipole moments. In uniaxial liquid crystals—like in the nematic and smectic A phase—only the component of the dipole moment which is parallel to the long molecular axis can be different from zero and
spontaneous polarization can arise only through "head to tail" ordering. The polarization is thus necessarily parallel to the nematic director $\mathbf{p}_n \parallel \mathbf{n}$.

In biaxial systems, like in the smectic C and smectic A phases and possibly in some cholesteric systems—Which are composed of chiral molecules, there may be a non-zero component of the molecular dipole moment normal to the long molecular axis. In such systems, as indeed observed, ferroelectricity may arise without "head to tail" ordering, if the molecules do not rotate around their long axis or if this rotation is biased.

As dipolar interactions by itself are too weak to produce ferroelectric ordering in the liquid, polarization can occur only if induced by liquid crystal-like ordering. Since polarization is not the true transition parameter the ferroelectricity that arises cannot be regarded as normal. Ferroelectric liquid crystals are thus improper ferroelectrics.

Frank's (29) view on microscopic symmetry stimulated the initial discovery that the spontaneous torsion and bending in the helix and the associated polarization, are all perturbations of the same order of magnitude; it seemed there must be some fundamental coupling of molecular chirality and polarization in a smectic C system. It is with this unusual combination
of symmetry properties that a liquid crystal composed of chiral molecules can be a ferroelectric.

In the crystalline case, a fundamental electrical and elastic instability is responsible for the appearance of the spontaneous polarization; the associated distortion of the crystal lattice is often extremely small. It is because the distortion is so small that the polarization is easily reoriented. However, in the liquid crystal, the fundamental forces responsible for the existence of the chiral phase (smectic C) have nothing to do with the spontaneous polarization. The molecular tilt angle, corresponding to the mechanical distortion of the crystal lattice, is very large, while the electrical polarization is a small secondary effect. This is just the opposite of the crystalline case and it has several consequences. For the thermodynamics of the chiral phase (smectic C), one can essentially ignore the presence of the polarization.

1.2.2 Hysteresis loop and domain structure of ferroelectric liquid crystals:

The hysteresis loops (30-34) observed in the liquid crystals (LC) are however due to the dynamics of the polarization reversal process and are by no means proof of a stable polarization in the absence of an electric field. The meaning of the term
"spontaneous polarization" applied to a LC is not quite the same as in the case of a crystalline ferroelectric. If the field decreases sufficiently slowly, the spontaneous polarization of LC sample is zero; this is one of essential differences between a liquid crystalline and a crystalline ferroelectric.

There are two electrical properties which are inherent only in the liquid crystal state: electric hysteresis and nonlinear conductivity which are to be reckoned with, while examining its ferroelectric behaviour.

Helicoidal structure in the liquid crystal plays the role of a domain structure in a crystalline ferroelectric to the extent that such an analogy is applicable; of course, the source of the helix is quite different from that of ferroelectric domains. It arises from local interactions rather than the minimization of the microscopic electrostatic field energy.

Sample as a whole should not exhibit polarization in the absence of an electric field due to mutual compensation of the spontaneous polarization of the twisted layers. An analogy can be suggested between the liquid crystal layers and ferroelectric domains in crystals, though the association is rather loose since there is no way to obtain a single domain liquid crystal sample in the absence of an external agent.
In a manner analogous to that of ferroelectrics the hysteresis loop in liquid crystals exists within a definite range of rate of change of field which is determined by the derivative of the field with respect to frequency; however, the frequency region for which hysteresis is observed is lower by some orders of magnitude than in ferroelectrics.

The conclusion can be drawn that the direction of polarization in liquid crystal is fixed; but, because the intermolecular interaction forces are rather weak, the external electric field acting on the polarization vector can orient the long axes of the molecule so that the direction of easy polarization will be along the field.

In crystalline ferroelectrics, in which there may be only a few easy axes for polarization, domain walls can have a high energy due mainly to crystalline anisotropy. The pinning of domain walls or the difficulty of nucleating new ones, is a major cause of hysteresis effects. In a single liquid crystal smectic C phase there is no easy axis for polarization in the layers and thus there are no spontaneous domains. Therefore in principle hysteresis is not possible. However, in polydomain samples or very thin ones contained between surfaces with strong alignment state, there can be pinning effects which produce at least
partial hysteresis. This is easily observed in experiments involving unwinding of the helix in the ferroelectric smectic C' phase.

1.2.3 Nematic phase to be ferroelectric?

Initially nematic liquid crystalline phase was thought to be susceptible to have ferroelectric properties. It was suggested that it possessed electrical properties which were similar to those of ferroelectrics (35, 36). Since then, a number of studies on the electro-optic behaviour of these materials have been performed and as a result a better understanding of their properties emerged. Amongst the earliest experimental papers in these liquid crystals are those of Kapustin and Vistin (37), Williams and Heilmeyer (38-45).

Williams has proposed a theory based on an analogy with domain formation in ferroelectrics in them. A careful study reported by Kessler et al (46) indicates that the remanent polarization and non-linearity of the low frequency impedance are due to electrochemical processes rather than due to ferroelectricity in the reported liquid crystals.

Kaye (47) has outlined a theory which may account for a number of the observed electro-optical effects. His theory is based on the relationship
between the Frank curvature strains and the related electric polarization in a nematic liquid. Meyer accepts the hypothesis that a nematic liquid crystal is nonpolar (and therefore not ferroelectric) in the absence of external forces. But he explains with the help of piezoeffect that \( \Delta P \) is seldom zero, so that the strained structures are usually space charged and the liquid crystalline curvature electric effects can be expected even though the structure has a centered symmetry.

Major and Coupé (48, 49) give convincing evidence that the forces predominantly responsible for parallel orientation in the nematic phase are the dipole-dipole dispersion forces. Theoretical (29, 70) and experimental (59-52) investigations of modulated ferroelectrics (nematic ferroelectrics) have been carried out over a number of years but until recently no reliably established results of nematic ferroelectric crystals have been found. Experimental attempts to verify the theoretical concept have been conflicting.

To conclude, ferroelectricity in liquid crystals has long been considered in the nematic phase. However, the experimental results in this phase have been interpreted not on the line of a true ferroelectric.

1.2.4 Ferroelectric chiral smectic C phase

Although ferroelectricity in smectic liquid crystals has been investigated by only few workers for nearly last
five years, the accumulated experimental data are
conclusive concerning the features of dipole ordering
in this system.

Recently symmetry arguments (53-58) and experi-
mental facts (13, 30-34, 54) offer evidence of dipole
ordering of the ferroelectric type in the smectic C phase.
In contrast to solid ferroelectric crystals, where the
main role is played by the long range dipole dipole in-
teraction, in liquid crystals the contribution from the
dipoles of the molecules to the total interaction energy
is small in comparison with the short range dispersion
forces. Therefore, ferroelectricity in the chiral smectic
phase of a liquid crystal can be due to the matched
inclination of the molecules and the hindering of their
rotation about their long axes (59-65).

The smectic C liquid crystalline phase is reported
to be ferroelectric when molecules are chiral (noncentro-
symmetrical) having a permanent dipole moment transverse
to their long molecular axes. In their high temperature
phase (smectic A) the molecules are rotating freely along
their long axes, which are oriented perpendicular to the
smectic layers, each layer corresponding to the point
group symmetry D∞. The transition to the ferroelectric
smectic C phase is induced by the two dimensional repre-
sentation when the point group symmetry of the layers is
monoclinic C2. The rather small difference in the
smectic A to smectic C* transition temperature; between chiral (ferroelectric) and reentrant (non-ferroelectric) phase. It shows that the transition is governed by intermolecular forces which produce the tilted smectic C* phase. Hence spontaneous polarization is a secondary ordering parameter. The spontaneous polarization is thus induced by the molecular tilt and the ferroelectric smectic C* liquid crystals are thus improper ferroelectrics.

Finally it can be said that the tilt angle of the molecules in the ferroelectric smectic C* phase is proportional to the spontaneous polarization; hence the piezo-coupling is important in these ferroelectric liquid crystals.

The molecular symmetry consideration leading to spontaneous polarization in the structure goes as follows—The environment of a molecule in a smectic C* structure is known to have monoclinic symmetry. If the molecule is chiral it has no mirror planes or centre of inversion of the monoclinic symmetries. Combining the molecular and environmental symmetry leaves the structure with only a two fold axis. Spontaneous polarization is parallel to this two fold axis. Therefore, sufficient conditions for polarity to occur in the smectic C* phase are that the molecules should be chiral and polar.

Once this symmetry criterion for ferroelectricity in liquid crystal is accepted, the search for appropriate
liquid crystal exhibiting smectic C\textsuperscript{+} phase at reasonable
temperature, and which could be modified slightly to be
chiral, becomes worthwhile for experimental exploration
of new ferroelectric liquid crystals.

Further, chiral tilted smectics, though cannot be
ferroelectric due to their centro symmetric structure,
but can host chiral guest molecules and provide a
parallel oriented dipolar structure, the resulting mixtures
can be expected to be ferroelectric. The chiral guest
molecules must fulfill some suitable conditions for the
mixture liquid crystal to be ferroelectric. In this
way even synthesis of new ferroelectric liquid crystal
is possible.

Kellor, Liebert and Strzelecki (13, 14, 66) worked
out the first ferroelectric liquid crystal with a chiral
smectic C\textsuperscript{+} phase, thereby remarkably confirming the initial
theoretical prediction (79-84). All the experimental
works published at this time have been made on this new
ferroelectric liquid crystal named p-desethyl benzilidene
p-amino-z methyl butyl cinnamate (KOSBAmC) with general
formula
\[
\text{CH}_3
\]

\[
\text{C}_n\text{H}_{n+1}\text{CO}_2\text{CH} = \text{N}=\text{CH}-\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

All these substituted materials with \(n\) greater
than 6 and less than 14 have been shown to exhibit
ferroelectricity (35-34).
Below the smectic C* phase a chiral smectic H* phase is obtained which should also display ferroelectricity (34). These smectic H* systems correspond to smectic C* systems with the layers behaving like 2-dimensional solids. In chiral systems there is again a helicoidal structure with the molecular tilt direction precessing around the normal to the layers and ferroelectricity is possible as in smectic C* system.

The temperature dependence of the spontaneous polarization in the smectic C* and smectic H* (S_C* & S_H*) phases is due to a rather slow process of the collective reorientation of dipolar molecules. Therefore, the temperature behaviour of the relaxation time for polarization near the phase transitions contains valuable information about their nature.

Up till now, the net volume polarization of the S_C* and S_H* chiral phases, produced by an untwisting external field interacting with the dipolar moments of smectic layers, has been considered to be ferroelectric. However, it has been shown theoretically (13, 67,68) that the macroscopic polarization can exist in mixtures of right and left hand rotating substances where the chirality is cancelled, but there is a finite value of the dipole moment of a smectic layer. Such a situation should occur for mixtures of molecules with approximately equal chirality but different transverse dipoles. Seresnev and
Table 1.1: Ferroelectric liquid crystals

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<tr>
<th>S. No.</th>
<th>Material</th>
<th>Structure</th>
<th>( T_c ) °C</th>
<th>Phase</th>
<th>( P_r ) C/cm²</th>
<th>Polar direction</th>
<th>Coercive field Kv/cm</th>
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General formula

\[
C_nH_{2n+1} \quad \text{CH} = N \quad \text{CH} = \text{CH} - \text{CO}_2 - \text{CH}_2 - \text{CH} - \text{CH}_2 \text{CH}_3
\]

\( n = 6 - 14 \)

Second order phase transition

1. DDBA-ABC (for \( n = 13 \))

- Monoclinic
- \( P_{2_1}/a \)
- p-1-decyloxy-2-nitrobenzylidene
- p'-amino-2-methylbutyl cinnamate.

- \( S_c^o = 95°C \)
- Helicoidal smectic C

- 10 \times 10^{-9} \text{ Polar direction}
- coincides with the two fold axis parallel to the smectic layer surface

2. DDBA-ABC (for \( n = 14 \))

- p-1-tetradecyloxybenzylidene
- p'-amino-2-methylbutyl cinnamate.

- \( S_c^o = 65°C \)
- Helicoidal smectic C

- 6 \times 10^{-9} \text{ Polar direction}

3. ODMA-ABC (for \( n = 12 \))

- p-1-decyloxy-2-nitrobenzylidene
- p'-amino-2-methylbutyl cinnamate.

- \( S_c^o = 75°C \)
- 1.2 \times 10^{-9} \text{ Polar direction}

4. GDBE-EC (for \( n = 8 \))

- p-1-decyloxybenzylidene
- p'-amino-2-methylbutyl cinnamate.

- 0.8 \times 10^{-9} \text{ Polar direction}

5. H-GABA-ABC (for \( n = 7 \))

- p-1-decyloxybenzylidene
- p'-amino-2-methylbutyl cinnamate.

- 0.5 \times 10^{-9} \text{ Polar direction}

6. Hx GABA-ABC (for \( n = 6 \))

- p-1-decyloxybenzylidene
- p'-amino-2-methylbutyl cinnamate.
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<tr>
<td>7</td>
<td>HOACPC</td>
<td>p-hexylxybenzylidene-4'-amino-</td>
<td>Monoclinic</td>
<td>S° = 75°C</td>
<td>Helicoidal</td>
<td>1.6x10^-8</td>
<td>Polar direction</td>
<td>coincides with</td>
<td>the two fold</td>
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<td>2-chloro-propyl cinnamate</td>
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<td>8</td>
<td>Ester Ferroelectric liquid</td>
<td>crystal</td>
<td>MBOPE, DTEA</td>
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<td>4(2-ethylbutoxy) benzyl ester</td>
<td>of 4-dexoxybenzoic acid</td>
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<td>9</td>
<td>Salicylidenquelines</td>
<td>(n = 7 - 10)</td>
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<tr>
<td>10</td>
<td>NOHB (doped with chiral guest)</td>
<td></td>
<td>4-n-monyloxy-4-α hexyl phenyl</td>
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<td>NOHB (0.3%w)</td>
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<td>NOHB (0.1%w)</td>
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<td>11</td>
<td>Non helicoidal ferroelectric</td>
<td>liquid crystal binary mixture</td>
<td>of DOBAMB + HOACPC</td>
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**Table - 1.1 continued**

(13) (72) (71) (69)
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<td>12. p-Azaxyanisole</td>
<td>Monoclinic</td>
<td>116-132°C</td>
<td>nematic phase</td>
<td>0.39x10^-6</td>
<td>10</td>
<td></td>
<td>(76)</td>
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\[
\text{CH}_3 \text{O} \begin{array}{c} \text{N} \end{array} \text{= N} \begin{array}{c} \text{O} \end{array} \text{OCH}_3
\]

13. p-Azoxysthenol | 137-168°C |   | 0.2x10^-6 | 2.9 |   | (74,75) |

\[
\text{C}_2\text{H}_5 \text{O} \begin{array}{c} \text{N} \end{array} \text{= N} \begin{array}{c} \text{O} \end{array} \text{OC}_2\text{H}_5
\]

14. p-Methoxycinnamic acid | T_{melt} = 175°C |   | 0.2x10^-6 | 2.9 |   | (74,75) |

\[
\text{pCH}_3 \text{O} \begin{array}{c} \text{CH} = \text{CH} - \text{COOH}
\]

hysterisis loop was observed in the nematic phase.

15. p-Butoxybenzole acid |   |   |   |   |   | (75,78) |

\[
\text{CH}_3(\text{CH}_2)_2 \text{CH}_2 \text{O} \begin{array}{c} \text{COOH}
\]

hysterisis loop was observed in the liquid phase.

16. Azobenzene | T_{melt} = 66°C | Liquid phase |   |   |   | (76) |

17. Azobenzene | T_{melt} = 35°C |   |   |   |   | (76) |
Linov (62) have most recently found that proper percentage of mixture of 40% CMB and 60% HOBAC have polarization two times more than that for pure CMB. Hence they managed to obtain untwisted ferroelectric liquid crystals by incorporating some non-mesogenic chiral dopant into the $S_{p}$ phase of opposite chirality. In this way a variety of ferroelectric liquid crystals can be synthesized by introducing chiral guest molecules with a transverse dipolar moment into a non-chiral tilted nematic phase.

Various known ferroelectric liquid crystals have been tabulated with important parameters in the Table no. 1.1.

1.3 Pyroelectricity in relation to Ferroelectrics:

Ferroelectrics form a subgroup of pyroelectrics. Jaffe et al have very clearly demarcated relationship between the ferroelectricity and pyroelectricity. Although all pyroelectrics have a dipole, it is not always possible to reverse the direction of spontaneous polarization in all of them with the electric field due to its structure or lower break down field. Thus spontaneous polarization of ferroelectrics is different from that in pyroelectric crystals depending on situation where the dipole net work within the crystal can be practically reversed. Even though all ferroelectrics are piezoelectrics and pyroelectrics, and all pyroelectrics are necessarily piezoelectric, yet pyroelectricity is basically distinct from
piezoelectricity as the two depend on different symmetry considerations i.e. one is polar and other simply lacks a center symmetry (86).

Usually in ferroelectric crystals there exists a non-polar (paraelectric) phase above the curie point. However, a few ferroelectric crystals like Rochelle salt also exhibit a lower curie point below which they exist in paraelectric phase. The paraelectric phase of a ferroelectric may be either polar or non-polar (87-89). Thus as such pyroelectric investigations should be undertaken in all ferroelectrics both below and above the curie point.

1.3.1 Pyroelectricity:

Crystals having a polar structure exhibit electric polarization when their temperature is changed. This phenomenon is known as pyroelectricity and arises out of the temperature dependence of the spontaneous polarization in these crystals (90). While all the ferroelectric crystals are necessarily pyroelectrics, the converse need not be true.

1.3.2 Pyroelectric coefficient:

Pyroelectric coefficient is defined as

\[ \varepsilon (\theta) = \frac{dT}{dt} \frac{d\theta}{T} \text{at constant stress} \]

It is a temperature derivative of the spontaneous polarization \( P_s \) in a crystal at constant stress \( T \) and electric field \( E \). Equation (1) can be also written as
\( \phi(\theta) = \frac{1}{A} \left( \frac{dq}{d\theta} \right) \)

where \( dq/d\theta \) is the change per unit change of temperature and \( A \) is the area of the specimen.

1.3.3 Symmetry and pyroelectricity:

Tsayama's principle suggests the crystal classes in which pyroelectricity can be exhibited. Quantitatively, the pyroelectric effect could be described by the equation

\[ \Delta A_i = P_i \Delta \theta \]

where \( \Delta \theta \) denotes the change in temperature, and

\( P_i (i = 1, 2, 3) \) are the changes in the component of polarization \( P \) in the three dimensional space and \( P_i \) are the corresponding pyroelectric coefficients (21).

The possible components of pyroelectric vector \( P \) in different polar crystal classes as follows:

**Triclinic**

**Class 1:** There is no symmetry restriction on the direction of \( P = (P_1, P_2, P_3) \). It will be decided by the structure and nature of chemical bonds.

**Monoclinic**

**Class 2:** \( P \) parallel to the diaz axis \((0, 3, 0)\)

**Class 3:** \( P \) can have any direction in the symmetry plane \((p_1, 2, 3)\)
orthorhombic

Class 2m2: p parallel to the diaz axis \((0,0,p_3)\)

Trigonal

Class 3: p parallel to the 3-fold axis \((0,0,p_3)\)

and \(3\bar{m}\):

Trigonal

Class 4

and \(4\bar{mm}\): p parallel to the 4-fold axis \((0,0,p_3)\)

Hexagonal

Class 6

and \(6\bar{mm}\): p parallel to the 6-fold axis \((0,0,p_3)\)

1.3.4 Primary, Secondary and Tertiary pyroelectricity:

Pyroelectricity is exhibited in ten polar classes 1, 2, \(1\bar{m}, 2\bar{mm}, 3, 3\bar{m}, 4, 4\bar{mm}, 6\) and \(6\bar{mm}\). The symmetry permits all the pyroelectric crystals to be piezoelectrics. There can be some additional contributions to pyroelectricity in the following way: during measurements, either the shape and size of the crystals can be kept fixed while heating or the crystal be free to expand with the temperature. Obviously the magnitude of the effect observed in the two cases will be different. In the first case the observed effect may be regarded as the primary pyroelectricity and in the second case, since the pyroelectric effect arises due to the variation
of piezoelectrically induced polarization through thermal strain, it is known as the secondary pyroelectricity. The secondary pyroelectricity is found to contribute substantially to the total effect depending on the situation. Hence for a free crystal the total pyroelectric effect could be written as

$$\varepsilon_{\text{total}} = \varepsilon_{\text{primary}} + \varepsilon_{\text{secondary}}$$

where \(\varepsilon_{\text{primary}}\) and \(\varepsilon_{\text{secondary}}\) denote the primary and secondary pyroelectric effects, respectively.

Alternatively, this can be written as

$$\varepsilon_{\text{total}} = \varepsilon_{\text{primary}} + \varepsilon_{\text{secondary}}$$

where \(\varepsilon_{\text{primary}} = \sum_{ijkl} d_{ijkl} \sigma_{ij} \varepsilon_{kl}\) and \(\varepsilon_{\text{secondary}} = \sum_{ijkl} \kappa_{ijkl} \sigma_{ij} \varepsilon_{kl}\).

Though secondary pyroelectricity is due to piezoelectricity, not all piezoelectric crystals exhibit secondary pyroelectricity which are polar. In addition, the uneven heating causes temperature gradients in the crystals which, through thermal expansions, give rise to
non-uniform stress and strains. This secondary pyroelectricity due to non-uniform heating is called the
tertiary pyroelectric effect. The tensiplial pyroelectricity refers to the production of quadrupole or higher
electric moments on heating.

1.3.5 Pyroelectricity in ferroelectric liquid crystals:

In ferroelectric liquid crystals the pyroelectric
effect is due to volumetric spontaneous polarization.
In ferroelectric liquid crystals pyroelectricity is
characterized due to strong temperature dependence of
polarization arising from thermal disorientation of
molecules. This reorientation of dipolar molecules is a
rather slow process and hence relaxation times of polari-
zation is relatively much more larger in comparison to
solid ferroelectrics. The relaxation time for polarization near the phase transitions contains further valuable
information, these investigations have been extensively
discussed by the USAR group ([5-7]).

Initial studies of pyroelectricity in liquid
-crystal was done by the group at Temple University led
by Labes ([6]). They demonstrated a pyroeffect in the
chiral smectic C phase of poled p-decyloxy benzylidene-
'anthro-3'-methyl butyl cinnamate. The effect known as
"thermal pseudo hysteresis", observed for the first time
in the smectic C phase of liquid crystal 4,4'-di-1-
-octyloxy azoxybenzene (1981) was explained by Nguyen
and Wrobel (94) as resulting from a pyroelectric phenomenon.
in the liquid crystalline structure. Later on, the group of Varesnev and Blinov (95-77) with the interest to investigate the dynamics of liquid crystal lattice investigated the kinetics of the pyroelectric current of a ferroelectric liquid crystal L-DOPA. They observed a high pyroelectric coefficient \(2 \times 10^{-9} \text{C/cm}^2/\text{C}^\circ\) in a smectic A liquid crystal phase when heated by Nd-glass-laser pulses.

Pyroelectric effect in nematic liquid crystal has been quoted by Chvyr'ov and Iachinov (98). The pyroelectric in pure \(2\text{H}n\) (4-ethoxybenzylidene 2-n butylicynoline) and \(C\text{H}2\) (4-cyanophenyl p-naphthoate) their nematic phases were studied by an He laser. They pointed out that, for nematic phases with negative dielectric anisotropy, pyroelectric coefficient is negative and for positive it is positive.

Possibilities of observing the pyroelectric effect in ferroelectric and nonferroelectric (under special conditions) liquid crystals have very recently been reviewed by Varesnev and Blinov (64). The temperature dependence of the volume pyroelectric co-efficient and spontaneous polarization \(P(\theta)\) are demonstrated for the chiral smectic A

and \(\pi\) phase of \(\text{C}\), \(\text{C}\), p-decylxybenzylidene-4' amino-2- methylbutyl cinchonanil \(\text{C}\), \(\text{C}\), (3-naphthoxy benzylidene-4' amino-3-chloro-propiol-cin acetate) and \(\text{C}\), \(\text{C}\), \(\text{C}\), \(\text{C}\), (4-p-acetylbenzoic) phenyl ester of 4-decylxy benzoic acid. The effect of impurities, particularly conductive ones, on the pyroelectric properties and polarization in liquid crystals has been discussed in detail.
As it has been stressed earlier that pyroelectricity which is the occurrence of spontaneous polarization in the crystalline phase with change of temperature as a prerequisite condition for the material to be ferroelectric; so also is the case with the liquid crystalline system. The pyroelectric behaviour in liquid crystal occupies a status of an important study in understanding the origin of spontaneous polarization and hence is an important characteristic of ferroelectric materials in the liquid crystalline system as well. The emphasis of the presented work has been mostly on these lines to understand ferroelectricity in liquid crystal.

1.4 Dielectric Relaxation in Organic Materials:

The ferroelectric transitions are basically of dielectric nature. Hence study of dielectric properties as a function of temperature and frequency has been one of the established codes of investigations in the study of ferroelectric materials.

The variation of the dielectric constant with frequency leads to the dispersion study. The dielectric dispersion is characterised as resonance or relaxation type to access the working of the ferroelectric mechanism. The particular material may have more than one dispersion frequency of both types; however, the one responsible for the ferroelectric mechanism can be understood from the temperature dependence study.
The dielectric loss or dissipation is also important because it has interesting relationship to some of the important ferroelectric properties whether they be hysteresis loop, non linearity, domains or their pyroelectric behaviour.

In majority of the ferroelectric materials, the dielectric study has been largely done, covering in the case of dispersion study the microwave and infrared absorption regions. Such relaxation studies have been dealt in detail in all reported organic ferroelectric materials and our emphasis will be only on the ferroelectric liquid crystals since specific features of ferroelectricity in liquid crystals give special emphasis in their relaxation studies. The dielectric absorption, giving the highlights of molecular motion of rotation/dissociable groups, give insight to understand the occurrence of spontaneous polarization in the ferroelectric liquid crystals.

Dielectric studies of ferroelectric organic materials have been extensively studied for example: Ca(\text{H}_2\text{O})_2\text{thiourea} (99); \text{CsCl}_3\text{H}_2\text{Cl}_2\text{Tetramethylammonium-trichloro-acurate family} (100,101); \text{Cu(CO}_3\text{)}_2\cdot\text{H}_2\text{O}

Capric formate tetra hydrate (102); \text{Ca}_2\text{P}\left(\text{PO}_4\right)_2\cdot\text{H}_2\text{O}_3\text{ family} (105,106); \text{CsClICO}_3\cdot\text{H}_2\text{O}_4\text{ Anionium non-chloroacetate family} (107,108); \text{K}_2\left(\text{NH}_2\text{CO}_2\text{H}_2\text{Cl}_2\text{O}_2\right)_2\cdot\text{H}_2\text{O}_4\text{ family}(107-112);
(152-155), \( \text{NH}_2\text{CH}_2\text{COO}^- \text{AgNO}_3 \) glycine silver nitrate (113), \( \text{NH}_2\text{CH}_2\text{COO}^- \text{HNO}_3 \) family; \( \text{Bi-glycine nitrate} \) (114-116); scheelite salt \( \text{Na}_2\text{H}_4\text{O}_6\text{S}_2\text{O}_7 \text{H}_2\text{O} \) family (117,118); (123,124-123) \( \text{LiH}_2\text{C}_2\text{H}_2\text{O}_6 \text{H}_2\text{O} \) family. Lithium amonium tartrate monohydrate (119) DMA (120-122) and polyvinylidene fluoride (123-151).

1.4.1 Dielectric studies in liquid crystals

The theory of dielectric anisotropy of nematic liquid crystals considers the main mechanisms of dipole polarization of the mesophase related to the rotation of polar molecules about the long and short geometrical axes. Some of them have been experimentally established and studied (166-173) in investigations of static and rotational properties of \( \text{LC} \) with both negative and positive dielectric anisotropy. The molecular structure of a nematic liquid crystal is fixed by only one principle of order: the long axes of the molecules are, on the average, parallel to a distinct direction. Because of the thermal motion, the long axes of the molecules oscillate around the preferred direction. From this principle of order there follows an anisotropy of all physical properties and this anisotropy is that of uniaxial crystal. The preferred direction is the optical axis of the liquid crystal.

In homogeneously ordered liquid crystals two principal dielectric constant can be measured i.e.
parallel ($\epsilon_{//}$) and perpendicular ($\epsilon_{\perp}$) to the symmetry axis of the liquid crystal. The two dielectric constants may also show entirely different relaxation behaviour. The principal dielectric constants, according to Maier and Maier (164), depend on the principal polarizabilities of the molecule, the permanent dipole moment and its direction with respect to the long molecular axis and the degree of order of the liquid crystal.

The mechanism of the dipole orientation in a nematic liquid crystal can be considered as a rotation of molecules around a transverse axis. This rotation must be very much more hindered than the other motions of rotation, for example, a rotation around the long molecular axis is essentially not hindered.

For liquid crystal 44'-di-n-octyloxy azobenzene, as measured by Maier and Maier (146) $\epsilon_{//}$ is larger than $\epsilon_{\perp}$, the difference amounts to a few per cent. At the transition point from the liquid crystalline to the actually liquid state the anisotropy vanished discontinuously. In the case of p-anisoyl anisole (167) there is a strong dipole moment that makes a large angle with the molecular long axis. Therefore $\epsilon_{//}$ is greater than $\epsilon_{\perp}$.

All compounds, have a principal dielectric constant $\epsilon_{11}$ which is larger than $\epsilon_{\perp}$. At higher frequencies and sufficiently strong electric fields, the preferred molecular orientation is in the direction of the field,
if there are no other orienting forces. With p-azoxyanisole, \( \varepsilon_{11} \) is smaller than \( \varepsilon_1 \). Here the preferred direction is perpendicular to the electric field. For p-hexyloxy azoxybenzene (170) in the frequency range 180 Hz to 4 MHz, \( \varepsilon_1 \) is not dependent on the frequency but \( \varepsilon_{11} \) shows a pronounced dispersion. The dispersion vanishes at the transition point.

With alkoxy derivatives of azobenzene (175), only the normal Debye dispersion region at microwave frequencies has been observed. With alkoxy derivatives of azoxybenzene (175), \( \varepsilon_1 \) shows again only the normal Debye dispersion region at microwave frequencies, but \( \varepsilon_{11} \) has an additional dispersion at very low frequencies in the radio-frequency region. This dispersion is due to the permanent electric dipole moment of the azoxy group, more exactly to its component parallel to the long molecular axis.

... SEC mixtures (176, 177) that form the mesomorphic state over a wide temperature range. \( \varepsilon_{11} \) is high and exhibits dielectric anisotropy owing to the strong polarity of their molecules.

Dielectric relaxation studies of 5BBA (p-methoxybenzylidene p-n-butyylaniline) is analysed in the metastable modification (173). Permittivity \( \varepsilon'(\omega) \) and losses \( \varepsilon''(\omega) \) are described by a skewed Davidson-Cole expression. A model is proposed by the author which assumes
correlation between the rotation of the dipolar methoxy group about the (O-C) bond of the molecule and conformational motions of the butyl group causing local fluctuations (defects) in the crystal lattice. The binary mixtures of DBOA with other nematogenic or non-nematogenic compound, their relaxational behaviour has been observed (179, 180). The both long range and short range intermolecular interactions in nematic phase increase anomalously near the transition.

1.4.2 Dielectric relaxation in ferroelectric liquid crystals:

Since the discovery of the ferroelectricity in the chiral smectic C phase of DDBAC (13) extensive studies have been done mainly on this material (15-21). The spontaneous polarization of this material was estimated to be much smaller than those in solid ferroelectrics, which was explained in terms of a rotation in molecule around its long axis and intramolecular rotation or vibration. The hindrance of a free rotation of a molecule around its long axis and intramolecular interaction caused by the chirality is considered to be essential for the appearance of ferroelectricity. Such ordering in the liquid crystal leads to interesting results in the dielectric studies.

Hoffmann et al. (31) carried out measurement of the electric permittivity $\varepsilon$ as a function of temperature throughout the frequency range from $5 \times 10^2$ to $1 \times 10^5$ Hz, where
in the phase C of DODABBC is found to depend strongly on the frequency between 20Hz to 20 kHz, below and above this range the frequency dependence vanishes. Relaxation time exhibits maxima for the transitions Sm A \rightarrow Sm C and Sm C \rightarrow Sm H. The increase in relaxation time in the C \rightarrow H transition is due to the increase in viscosity, whereas that in the C \rightarrow A transition can be interpreted as due to the increase in pitch of the helix immediately preceding the phase transition, as the relaxation time is proportional to the second power of the pitch. In the phase A the relaxation time falls steeply to very small values.

Dielectric properties of several ferroelectric liquid crystals and their mixture and influence of the pressure on them, has been studied in detail by Uemoto and Yoshina et al. (23, 30, 32-34) on compounds of the series of L-p-alkoxy benzylidene-p' amino-2-methylbutyl-cinnamate (L-pDORAMBC), with alkoxy chain length n between 6 and 14 (6 \leq n \leq 14) they are (L-pDORAMBC, L-pDORAMBC, L-pDORAMBC, L-pDORAMBC, L-pDORAMBC). They have shown that the dielectric constant is maximum for DODABBC (n = 10) and also the spontaneous polarization is maximum. Beyond and below (n = 10), dielectric constant decreases. In the case of shorter alkoxy chain n < 10, the spatial hindrance and the interaction between neighbouring molecules are small and the rotation of molecule around its long axis becomes easier; therefore the spontaneous
polarization becomes smaller and even ferroelectricity disappears \( n < 6 \). It clearly shows that not only chirality of molecule but also alkoxy chain length play an important role for the hindrance of the three rotation of the molecule around its long axis and which seems essential for the appearance of ferroelectricity. For \( n > 10 \) molecular number density should decrease and therefore inter-molecular distance should increase, resulting in the smaller spontaneous polarization.

Frequency dependence of dielectric constant, in DNOBAMBC \( (n = 12) \) in smectic A phase, shows no change against frequency between 50 Hz to 200 kHz. The difference of \( \varepsilon \) between smectic A and C* phases at 100 Hz is considered to be due to the contribution from spontaneous polarization in the smectic C* phase. Dielectric studies of another ferroelectric liquid crystal L-DODACPC have been compared with D-DODACBC by Uemoto and Yoshino (26). The maximum dielectric constant in L-DODACPC is larger by more than factor of 5 compared with that in D-DODACBC.

The low frequency order parameter fluctuation spectrum of chiral DODA BC has been studied by Blinc et al. (187) at the ferroelectric smectic A \( \rightarrow \) C* transition by dielectric relaxation spectroscopy. Above \( T_c \), the dielectric constant changes slightly with frequency and temperature, while below \( T_c \) it is possible to observe a distinctive dispersion and temperature dependence. The
low frequency of the polarization fluctuation spectrum is expected to have a soft mode behaviour above $T_c$; while below $T_c$, it should be the superposition of the soft mode part and the Goldstone mode part. Normal modes of distortion induced by A.C. field on ferroelectric liquid crystal close to its transition has been analytically calculated by Martinot-Lagarde (182) and Durand. These normal modes are superpositions of electric polarization and angular molecular distortions.

From the foregoing earlier investigation on ferroelectric liquid crystals it is obvious that the dielectric study constitutes an important investigation in the understanding of ferroelectric behaviour and hence it was contemplated to extend it in materials of our investigation in the following chapters.
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