A Thesis

On

“NANO PARTICLES DISPERSED LIQUID CRYSTAL COMPOSITES”

In

Partial fulfillment of the requirements for the award of the degree

Of

MASTERS IN TECHNOLOGY

In

MATERIALS SCIENCE & ENGINEERING

Submitted By

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CERTIFICATE

This is to certify that the thesis entitled “***Nano Particles Dispersed Liquid Crystal Composites***” which is being submitted by ***DEEPIKA SHARMA*** in Partial fulfillment of the requirements for the award of the degree of ***Masters in Technology (M.Tech.) in Materials Science and Engineering*** of Thapar University, Patiala (India), is a record of the study conducted by her under my supervision and guidance and that no part of this thesis has been submitted for the award of any other degree.

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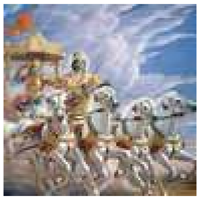

the teachers who inspired me

the parents who nurtured me

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ABSTRACT

Nano particles dispersed ferroelectric liquid crystals are playing very vital role in the development of new materials for improving display devices in industries. Nano particles dispersed ferroelectric liquid crystals have high dielectric constant, fast switching response, and large electro-optic coefficient, making them ideal for memories, capacitors and display devices etc. In this work, an attempt has been made to understand the influence of nano particles of carbon and barium ferrite on dielectric and morphological properties of FLC and how the level (wt/wt%) of nano particles concentration effect the switching response and transition temperature of FLCs. Introduction to the fundamentals of ferroelectric liquid crystals and effect of nano particles on properties of FLC has been reviewed.

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CHAPTER 1

Introduction

1.1 REVIEW

Composites based on liquid crystal (LC) materials have attracted much attention over last number of years because of their unique electro- and magneto-optic properties and novel display applications. Typical examples of these systems are polymer dispersed liquid crystals [1], suspensions of aerosils in LC matrices [2] and suspensions of nanotubes in ferroelectric LCs [3, 4]. The inclusions in known composite LC systems produce director distortions that extend over macroscopic scales. A new approach, however, proposed recently [5] is based on the idea of controlling the properties of the composites by adding a low concentration of nano particles into a LC matrix. These dilute nano suspensions are stable due to the weak interactions of the nano particles at low concentrations. The nano particles are so small that they do not disturb the LC orientation and thus macroscopically homogeneous structures are obtained. At the same time, the nano particles are sufficiently large to maintain the intrinsic properties of the materials from which they are made (e.g. ferromagnetism or ferroelectricity) and share these properties with the LC matrix due to anchoring with the LC. In particular, it was found that embedding nano particles in a ferroelectric liquid crystal at a low volume concentration (0.1%) did not change the elastic and anchoring properties of the LC, but did result in an enhanced dielectric response. In addition, the suspension exhibited an unusual linear response to the electric vector; the direction of the director reorientation was determined by the sign of the applied electric field.

Here we report studies of the dielectric properties of a liquid crystal containing nano particles of carbon and barium ferrite in very low concentration. We found that embedding the nano particles in a LC results in changes of the dielectric spectra caused by the strong interaction between LC and nano particles. Obtaining stable and uniform alignment of liquid crystal (LCs) on a macroscopic scale is essential to the fabrication of high-quality liquid crystal displays (LCDs). Typically, alignment involves modification of a solid substrate such that its interface with the LC has some anchoring action that results in either planar (tangential) or homeotropic (perpendicular) orientation of the LC director (symmetry axis) with respect to the interface. Such modification is carried out on a substrate having an electrically conductive layer (usually indium tin oxide or ITO-coated glass) for electric-field-induced reorientation of the director which, in turn, results in a variation in the transmitted light intensity. Nano-composites (from a fraction of a nanometer to about 100 nm) are at the confluence of the smallest of human-made devices and the largest molecules of living systems. At this dimension scale, nano particles embedded in a liquid crystal do not significantly perturb the director field in the liquid crystal and interaction between the nano particles is weak. However, the nano particles share their intrinsic properties with the liquid crystal matrix due to alignment and anchoring with it. For instance, it was recently reported that dispersing low concentration of submicron nano particles in a ferroelectric liquid crystals enhance the dielectric response and induces a linear response to the electric vector E in a ferroelectric liquid crystals [6]. In contrast to molecular additives, these tubes dispersions substantially lower the operating voltage of liquid crystals displays and related devices. Herein, we explore the potential of self assembled nano particles bundles as an alignment substrate for liquid crystals [7]. Since their discovery [8], nano particles have received immense attention across many disciplines by virtue of their unique structure and properties, as well as possible applications as nano-sensors and devices. Applications of interest include electron-emitting panel displays [9], single-molecular transistors in microelectronics [10], artificial muscles [11], and molecular filtration membranes [12]. An essential prerequisite for realizing the aforementioned applications centers on the fabrication of aligned CNT which has been a focused area of recent research efforts [13-18]. Alignment of nano particles with the aid of ferroelectric liquid crystals is an alternative approach in which the CNT molecules were found to orient parallel to the director of a ferroelectric solvent [19] observed molecular alignment was attributed to liquid crystal-induced alignment of the nano particles.

1.2 What are liquid crystals?

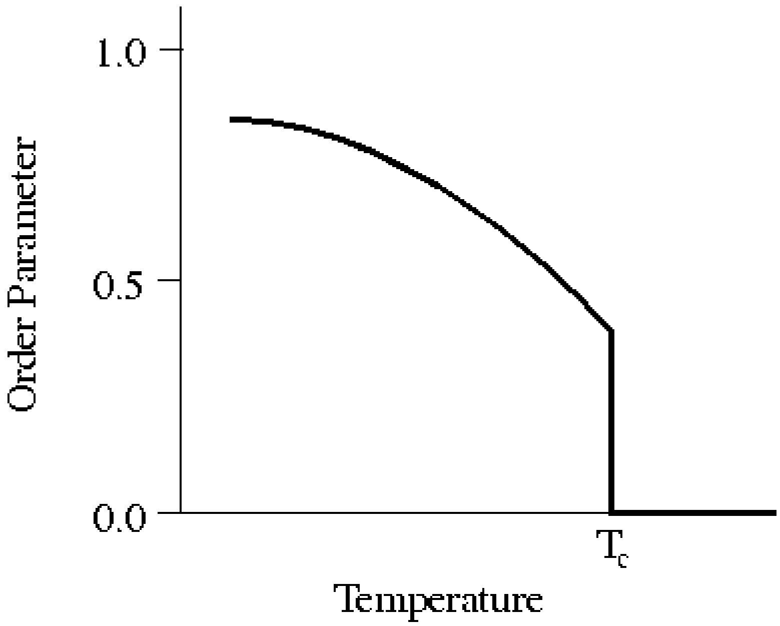
In nature, the borders between the different categories of materials (matter) are not well-defined. Ordinary fluids are isotropic in nature: they appear optically, magnetically, electrically, etc. to be the same from any perspective. Although the molecules which comprise the fluid are generally anisometric in shape, this anisometry generally plays little role in anisotropic macroscopic behavior (aside from viscosity). There are many interesting candidates for study including polymers, micelles, microemulsions and materials of biological significance, such as DNA and membranes. Although all of them very interesting this introduction will focus on liquid crystals. Liquid Crystals have the ordering properties of solids but they flow like liquids. In 1888, Friedrich Reinitzer credited for the first systematic report of the phenomena and reported his observations when he prepared cholesteryl benzoate (the first liquid crystal). However those liquid crystals were not suitable for any commercial usage, and it is only 25 years ago since the first material suitable for electronically driven displays, was developed. The first room-temperature nematic liquid crystal was observed in late 1960s. Occasionally in homologous series the temperature range could reach from –40 to +100^{0}C, these mixtures were very unstable and possessed a negative dielectric anisotropy not useful in the twist cell. The major breakthrough came when cyanobiphenyl materials were discovered a few years later. The more stable phase had a large positive dielectric anisotropy as well as a strong birefringence nearly ideal for the twist cell. During the year 1970 and 1980, several liquid crystal compounds and phases were discovered primarily by the industry.

Order Parameter

The description of liquid crystals involves an analysis of order. To make this quantitative, an orientational order parameter is usually defined based on the average of the second Legendre polynomial:

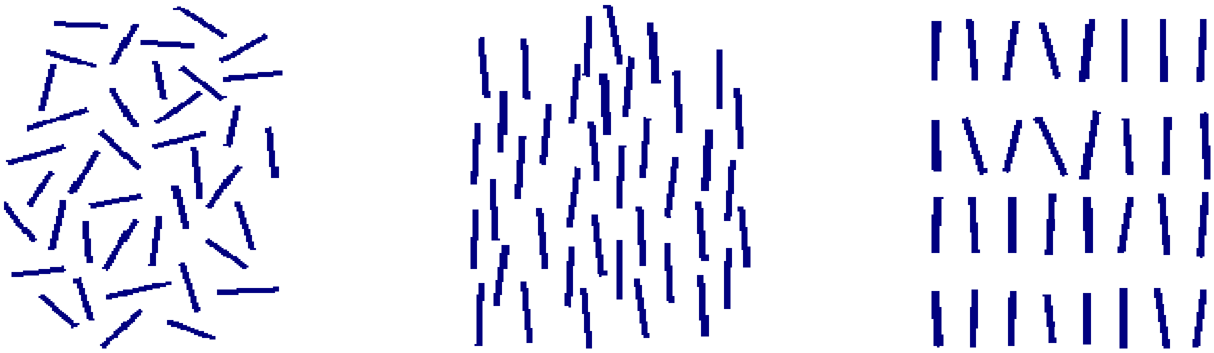
$$S = \langle P_2(\cos\theta) \rangle = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle$$

where θ is the angle between the mesogen molecule axis and the local director (which is the 'preferred direction' in a liquid crystal sample). This definition is convenient, since for a completely random and isotropic sample, S=0, whereas for a perfectly aligned sample S=1. For a typical liquid crystal sample, S is on the order of 0.3 to 0.8, and generally decreases as the temperature is raised. In particular, a sharp drop of the order parameter to 0 is observed when the system undergoes a phase transition from an LC phase into the isotropic phase. The order parameter can be measured experimentally in a number of ways. For instance, diamagnetism, birefringence, Raman scattering, NMR can also be used to determine S. Temperature is in degree Celsius.



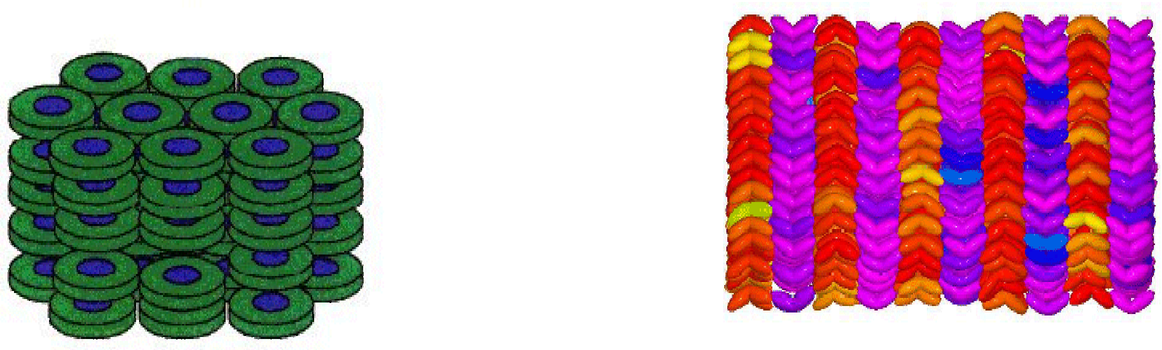
One could also characterize the order of a liquid crystal using other even Legendre polynomials (all the odd polynomials average to zero since the director can point in either of two antiparallel directions). These higher-order averages are more difficult to measure, but can yield additional information about molecular ordering. Then a smectic liquid crystal is obtained. In smectics, the orientation is fixed and the movement is limited to layers.

Fig1.1 represents arrangement and ordering of molecules (a) Isotropic (b) Nematic (c) Smectic



(a) Isotropic (b) Nematic (c) Smectic

Apart from the cigar shaped molecules some more complicated shaped liquid crystals are illustrated in the figure below. Fig1.2(a) represents a discotic liquid crystal stacked in a columnar phase. Figure1.2 (b) illustrates the stacking of banana shaped liquid crystals.



(a) Discotic shaped

(b) Banana shaped

Fig1.2 represents molecular stacking arrangement in (a) Disc shaped (b) Banana shaped systems

Effect of Chirality

Chiral mesogens usually give rise to chiral mesophases. For molecular mesogens, this means that the molecule must possess some form of asymmetry, usually a stereogenic center. An additional requirement is that the system not be racemic: a mixture of right- and left-handed versions of the mesogen will cancel the chiral effect. Due to the cooperative nature of liquid crystal ordering, however, a small amount of chiral dopant in an otherwise achiral mesophase is often enough to select out one domain handedness, making the system overall chiral. Chiral phases usually have a helical twisting of the mesogens. If the pitch of this twist is on the order of the wavelength of visible light, then interesting optical interference effects can be observed. The chiral twisting that occurs in chiral LC phases also makes the system respond differently to right- and left-handed circularly polarized light. These materials can thus be used as polarization filters. It is possible for chiral mesogens to produce essentially achiral mesophases. For instance, in certain ranges of concentration and molecular weight, DNA will form an achiral line hexatic phase. A curious recent observation is of the formation of chiral mesophases from achiral mesogens. Specifically, bent-core molecules (sometimes called banana liquid crystals) have been shown to form liquid crystal phases that are chiral. In any particular sample, various domains will have opposite handedness, but within any given domain, strong chiral ordering will be present. The appearance mechanism of this macroscopic chirality is not yet entirely clear. It appears that the molecules stack in layers and orient themselves in a tilted fashion inside the layers. These liquid crystals phases may be ferroelectric or anti-ferroelectric, both of which are of interest for applications.

1.3 Electric and Magnetic Field Effects

The response of liquid crystal molecules to an electric field is the major characteristic utilized in industrial applications. The ability of the director to align along an external field is caused by the electric nature of the molecules. Permanent electric dipoles result when one end of a molecule has a net positive charge while the other end has a net negative charge. When an external electric field is applied to the liquid crystal, the dipole molecules tend to orient themselves along the direction of the field. In the fig1.3, the black arrows represent the electric field vector.

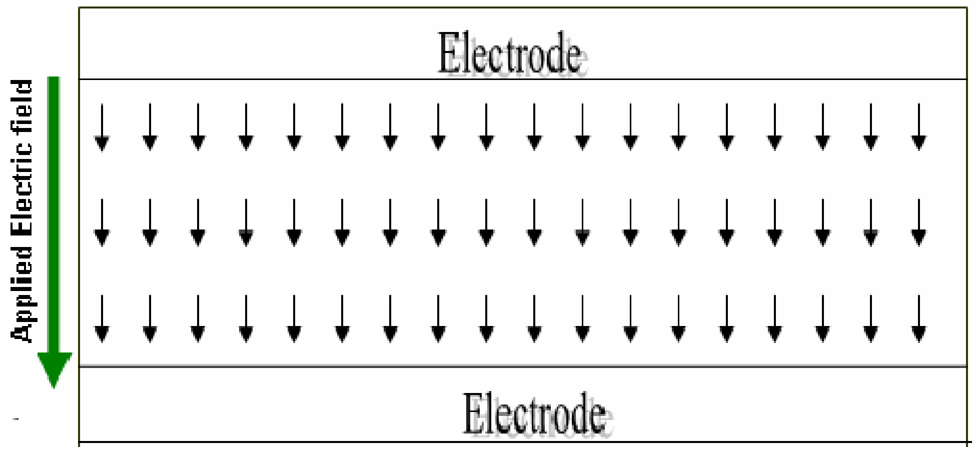


Fig 1.3 Effect of external electric field on liquid crystals

Even if a molecule does not form a permanent dipole, it can still be influenced by an electric field. In some cases, the field produces slight re-arrangement of electrons and protons in molecules such that an induced electric dipole results. While not as strong as permanent dipoles, orientation with the external field still occurs. The effects of magnetic fields on liquid crystal molecules are analogous to electric fields. Because magnetic fields are generated by moving electric charges, permanent magnetic dipoles are produced by electrons moving about atoms. When a magnetic field is applied, the molecules will tend to align with or against the field.

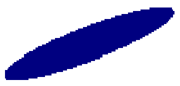
1.4 **Why are liquid crystals are so interesting?**

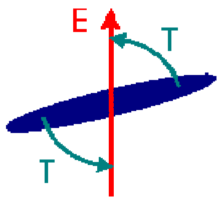
These materials are anisotropic. Not only in their shape, but also in all kinds of optical, electrical and magnetic parameters. It differs in the direction along the director of the molecules than in the plane perpendicular to it. Two interesting phenomena are the following :

- the reorientation of the molecules in an electric field
- optical birefringence of the molecules.

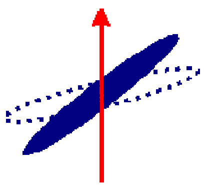
Reorientation of the molecules in electric fields

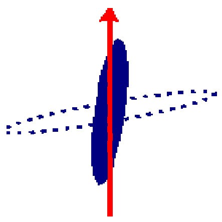
If the dielectric constant is larger in the direction along the molecule than in a direction perpendicular to it, one speaks of positive anisotropy. When a molecule with such a characteristic is brought in a sufficiently strong electric field, the director tends to align parallel to the electric field. Originally the orientation is almost flat. When an electric field with direction E is applied (represented in red), a torque T (represented in green) due to the dielectric anisotropy, acts on the molecule. The torque tends to align the molecule parallel to the field. When the field is strong enough, the molecule will be almost parallel to the field.


Original orientation



Situation in electric field


Result electric field


Result strong electric field

Switchable birefringence

A medium with a refractive index depending on the direction of propagation is called a birefringent medium. Because the director can be controlled using an electric field, a liquid crystal is a controllable birefringent medium. Birefringence is important for modifying and controlling the polarization of light propagating through the medium. To understand and calculate the propagation of light with an arbitrary polarization through a birefringent medium, the electric field vector is introduced. Light can be seen as an electric field described by a wave vector in each point. At a certain time and location, the direction and the length of the vector correspond with the direction and magnitude of the electric field. Generally each ellipsoidal polarization can be decomposed as a superposition of linear polarizations along two perpendicular axes. In an isotropic medium, both linear polarizations move with the same speed. In birefringent media, the situation is more complicated. The plane in which the ellipse rotates is no longer perpendicular to the propagation direction. The ellipse has to be decomposed into two linear polarizations along the ordinary and the extra-ordinary axis of the medium. Along these two directions, the two linear polarizations in which the ellipse is decomposed will feel a different refractive index and so they will propagate with a different speed. This is illustrated in fig1.4

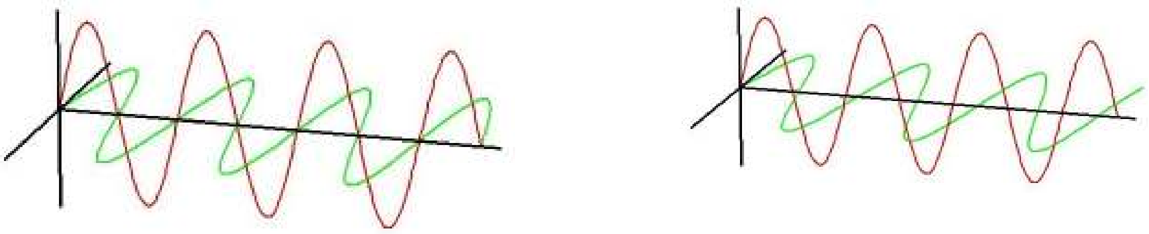
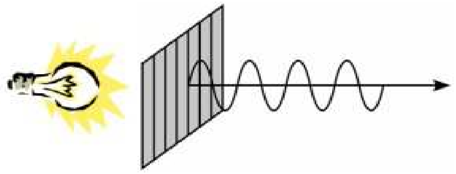
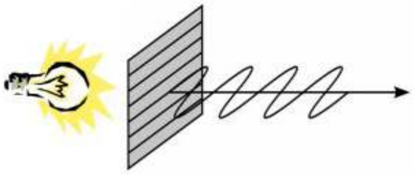


Fig1.4 (a) Isotropic Medium (b) Birefringent medium

In the isotropic medium, the two parts propagate with the same speed. Combining the two parts back together will result in the same polarization ellipse as the original one. In birefringent media, the two propagate with a different speed due to the difference in refractive index along these two axes. At the end of the medium the phase difference between the two oscillations has changed, which will result in a different polarization ellipse.



Polarizer with vertical transmission axis



(b) Polarizer with horizontal transmission axis

A polarizer (an extra layer needed to build a liquid crystal display) is a special type of birefringent layer. The ordinary wave propagates through the medium unmodified, whereas the extra-ordinary wave is absorbed in the medium. An arbitrary wave entering such a medium will result in a linearly polarized wave at the back of the medium. In the picture above the effect of a polarizer is illustrated for two different orientations of the absorbing direction.

1.7 Ferroelectric Liquid Crystal

The Nematic and Smectic A liquid crystal phases are too symmetric to allow any vector order, such as ferroelectricity. The tilted smectics, however, do allow ferroelectricity if they are composed of chiral molecules. Examples are given figure 1.11A and 1.11B

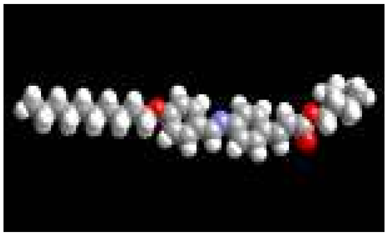


Figure 1.1A – DOBAMBC

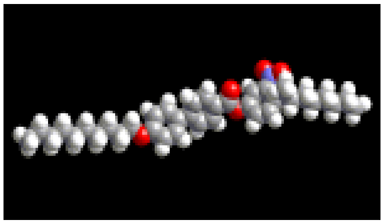


Figure 1.11B - W 314

Ferroelectric liquid crystals also exhibit a sponteous helixing of the polarization, so that over macroscopic distances (a few microns) the polarization averages to zero. Since the coupling of the polarization to applied fields is linear in the field, this means that Ferroelectric liquid crystals can be made to switch quickly (typically within a few microseconds) and in a bipolar manner. This makes Ferroelectric liquid crystals ideally suited to electro-optic applications.

1.8 Carbon Nano Tubes and Ferrites

Carbon Nano Tubes

Carbon nanotubes (CNT) are tiny cylindrical carbon structures with a diameter in the range of nanometers (10-9 meters). Structure of a nanotube consists of one cylinder or more coaxial cylinders of graphene sheet placed between two halves of a fullerene molecule (buckyball). Certainly we knew the two types of naturally occuring all-carbon allotropes with crystalline structure-

- covalent bonded diamond
- graphite (hexagonal structure)

Nanotubes are fundamental new structures, containing carbon atoms. The breakthrough in carbon science came from experiments on clusters formed by laser vaporisation of graphite, which finally yields to the discovery of Carbon Nanotubes by Iijima in the NEC-laboratories (Japan, 1991) by inspecting the cathodes after graphite arc vaporization. Carbon nanotubes (CNTs) are allotropes of carbon. A single wall carbon nanotube is a one-atom thick sheet of graphite (called graphene) rolled up into a seamless cylinder with diameter of the order of a nanometer. This results in a nanostructure where the length-to- diameter ratio exceeds 10,000. Such cylindrical carbon molecules have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of materials science. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat.

Single-walled nanotubes

Most single-walled nanotubes (SWNT) have a diameter of close to 1 nanometer, with a tube length that can be many thousands of times longer. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices (n,m) called the chiral vector. The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If m=0, the nanotubes are called "zigzag". If n=m, the nanotubes are called "armchair". The terms "armchair" and "zig-zag" refer to the arrangement of hexagons around the circumference otherwise, they are called "chiral", meaning that it can exist in two mirror-related forms as shown in figure z.

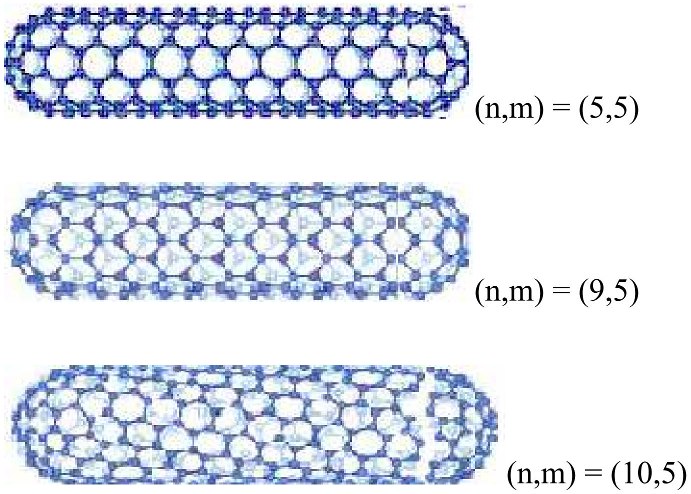


Fig. 1.13 The first two of these, known as “armchair” (top) and “zig-zag” (middle) have a high degree of symmetry. The third class of nanotube is known as chiral (bottom).

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 (MWNT) variants. Single-walled nanotubes 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 SWNTs can be excellent conductors [26]. One useful application of SWNTs is in the development of the first intramolecular field effect transistors (FETs).

Multi-Walled Nanotubes

Multi-walled nanotubes (MWNT) consist of multiple layers of graphite rolled in on them 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, e.g. a (0, 8) single-walled nanotube (SWNT) within a larger (0,10) single-walled nanotube as shown in figure D. 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, approximately 3.3 Å. The special place of double-walled Carbon Nanotubes (DWNT) must be emphasized here because they combine very similar morphology and properties as compared to SWNT, while improving significantly their resistance to chemicals.

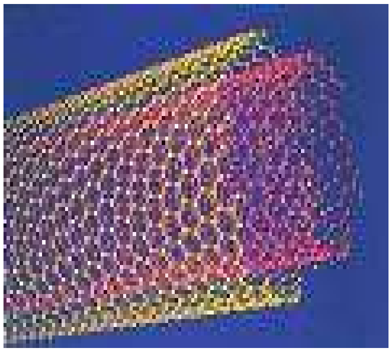


Fig. 1.14 Typical structures of multiwalled nanotubes.

Ferrites

Ferrites are magnetic materials. They come in the category of soft magnetic materials and are used in applications requiring frequent reversals of the direction of magnetization. Under ferrites, we are using nano particles of Barium Ferrite.

1.9 AIM OF THE THESIS

In the frame of this thesis, insights into the fundamental problems in the fabrication of Nano particles- based composite are presented. We find that embedding the nano particles in a LC results in changes of the dielectric spectra of the matrix, caused by the strong interaction between LC and nano particles. Thus in our thesis we will concentrate on the influence of nano particles on the dielectric and morphological properties of FLC.

CHAPTER 2

2.1 REVIEW

In the past more than three decades, material scientists have been exploring novel materials for applications in various electro-optical control and display devices such as optical shutters, switchable privacy windows, and reflective color displays. Ferroelectric liquid crystal (FLC) and nano particles (NPs) dispersed ferroelectric liquid crystal (NPDFLC) is a class of materials, normally prepared by sonication of an initially homogeneous solution of liquid crystal (LC) and nano particles. Therefore the selection of materials plays an important role on the performance of NPDFLC devices. The selections of materials in the present study has been made on the basis of their physical properties e.g. homogeneous mixing of NPs and liquid crystal, dispensability of NPs in liquid crystals, their purity, and the most important is the nano particles concentration in NPDFLC devices. For the preparation of CNT dispersed ferroelectric liquid crystal films by sonication method, several factors, i.e. time duration of sonication, concentrations of liquid crystal, concentration of CNTs and the size of the spacer, were adjusted. Nano Particles (NPs) as homogeneous materials found a wide practical application. Their composites with other materials, in particular, with liquid crystals (LCs), are of growing interest from scientific and technological points of view. A number of publications appeared recently in which properties of the NPs dissolved in LCs and properties of NPs film–LC interfaces were studied. Previous studies showed that the NPs are difficult to dissolve in LCs. They cannot form stable solutions, since solid NPs easily aggregate even at small concentrations in LC. In the present work, we report on the formation of NPs–LC systems stable in time. Frequency dependence of complex dielectric permittivity was studied to analyze how the properties of each component of the composite can influence dielectric parameters of the whole system.

2.2 MATERIALS

In the present work, the liquid crystal mixture and liquid crystals used in our experiments were commercially available ferroelectric liquid crystal mixture namely SCE13, which has comparatively large dielectric anisotropy, and large temperature range over which the different phases exist. The nano particles used in the experiments were multi wall carbon nano tubes with dimensions 110-170 nm, length between 5-9 micron and purity of 90+ % and barium ferrite with dimensions 5-15nm and purity of 99+%.

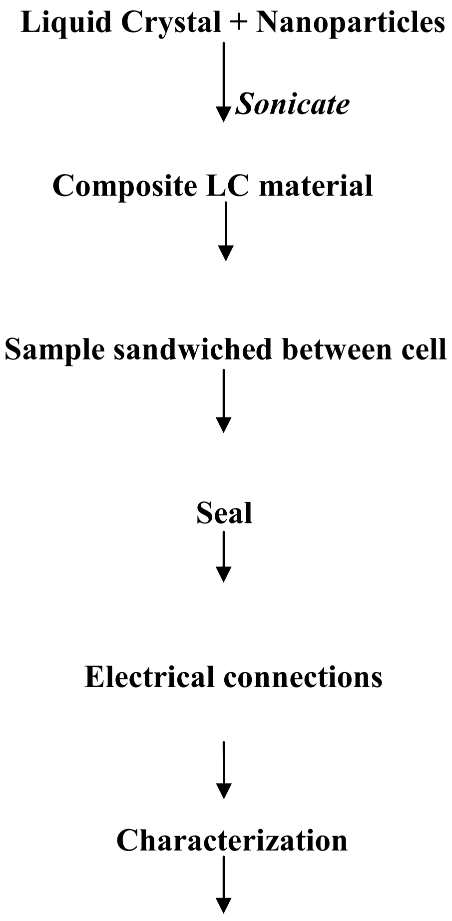
2.3 PREPARATION OF SAMPLE CELLS

Ferroelectric liquid crystal (FLC) and nano particles dispersed liquid crystal (NPDLC) sample cells were prepared using conducting indium tin oxide (ITO) coated glass substrates. Glass substrates were procured from Bharat Electronics Limited (BEL), Bangalore. Some commercial cells obtained from M/S Linkam Instruments, UK were highly transparent with resistivity of the order of few 140-180 ohm-m. The characterization with respect to morphological and dielectric studies etc was carried out in aligned and unaligned sample cells. Out of the two basic forms of alignment for liquid crystalline compounds or mixtures i.e. the homeotropic and homogenous [28-32], we used homogenous alignment method. In this method constituents molecules of LC phase are oriented parallel 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 thickness 5µm. These two glass plates were sealed with an adhesive. The electrodes were connected at the ITO coated substrate surface of the cell using indium (metal) ingot to obtaining better contact.

2.4 Preparation of NPs dispersed ferroelectric liquid crystal samples

To achieve a finer dispersion of NPs, sonication was applied to the NP mixture. The cell gaps were maintained with mylar spacer between the substrates in all the samples. The mixture is then sandwiched between indium tin oxide (ITO) coated glass substrates by capillary action, giving a sample thickness of 5 μm. The sample cells were sealed by an adhesive. The complete methodology of samples preparation is shown in Fig. 2.1 in the form of flow chart. An assembly of liquid crystal cell in empty and filled state is shown in Fig. 2.2 .After sealing and curing, the samples were placed in a LINKAM temperature programmer cum hot-stage. The optical micro-texture and nano particles dispersion were viewed at a magnification of 10X through Olympus polarizing microscope fitted with charge coupling device (CCD) camera. The NPDLC morphology, their dispersion is detected and acquired on a P IV computer using Linksys and RTVMS software.

Fig. 2.1 A flow chart for the preparation of CNTs dispersed ferroelectric liquid crystal samples.



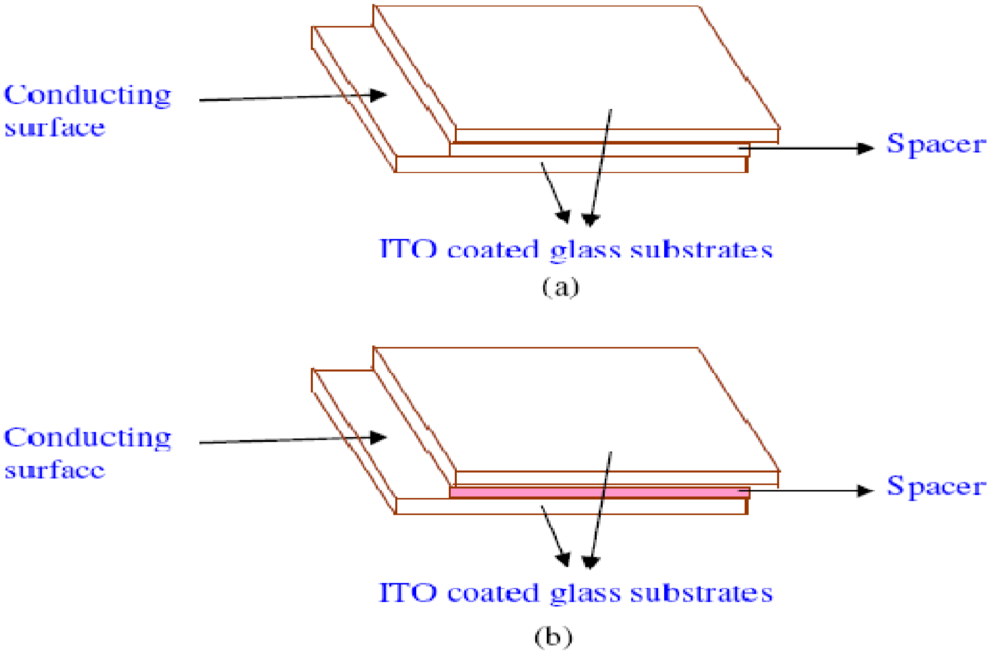


Fig. 2.2 An assembled (a) empty (b) filled liquid crystal cells

2.5 Provisional Techniques

In order to study the liquid crystal morphology and phase transition temperatures, Olympus polarizing microscope (Model- BX51P) and Linkam temperature programmer cum hot stage (Model TP94 and THMS 600) were used. The electric field was applied to the sample through Scientech function generator (Model ST 4060), Philips function generator (Model FG8002). The microscopic optical textures were captured through the charge coupling device (CCD) digital camera (Olympus DP 12 JAPAN) fitted on polarizing microscope and interfaced to a computer. A block diagram of our experimental set-up for the investigation of optical textures, electro-optic properties and other parameters of liquid crystal is shown in Fig. 2.3 The temperature of the NPDFLC sample cell was controlled using temperature controller interfaced with computer through RS232 port and the output response as a function of field was recorded on a Tektronix Oscilloscope (Model TDS2024). Uniform dispersion of nano particles in the FLC and all the optical textures were viewed under crossed polarizer at a total magnification of10X

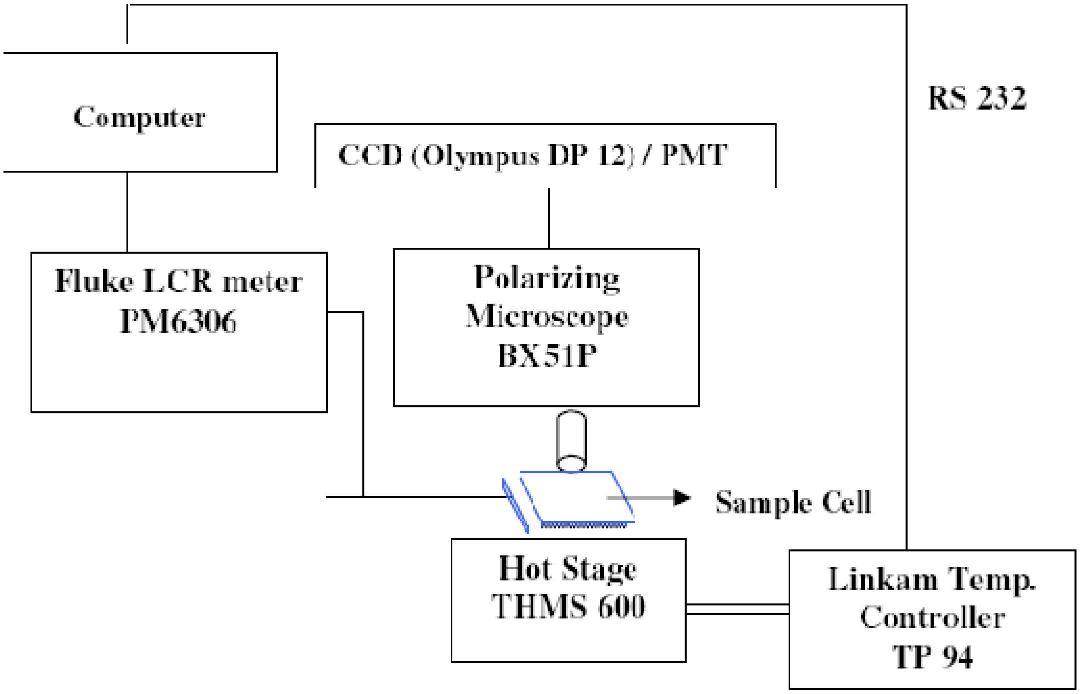


Fig. 2.3 Block diagram of the experimental set-up to study electro-optical properties.

Optical polarizing microscopy

The optical studies observed in ferroelectric liquid crystal and NPs dispersed ferroelectric liquid crystals investigated using an Olympus optical polarizing microscope (Model BX51P) at a magnification of 100X under crossed polarizers using long working distance objective lens. The optical micro-textures of LC materials were also investigated as a function of temperature, voltage and other physical parameters.

Temperature programmer along with hot stage

In thermal microscopy studies, we used Linkam temperature programmer TP94 and hot stage THMS 600. The TP94 is specifically designed for precise temperature control of the Linkam heating/freezing stages. 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. The temperature range is –196 ^{0}C to 600 ^{0}C. Heating or cooling rates can be changed almost instantly using the three rate keys. The heat ranges are from 0.1 to 0.9 ^{0}C/min at 0.1 degree intervals from 1.0 to 9.^{0}C/min at 1.0 degree intervals and from 10 to 90 ^{0}C 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.

Dielectric measurements

The dielectric measurements were carried out using a programmable automatic RCL meter (FLUKE PM 6306) in the frequency range 50Hz to 1MHz. The cell was calibrated using air and benzene as standard references. The frequency and bias dependence of the real and imaginary parts of the complex dielectric permittivity have been studied in detailed at room temperature. The dielectric properties of the NPDFLC were made in the presence of applied voltages that produced alignment (and, therefore, optical switching) of the LC phase. Dipole relaxation and ion-conduction-related processes were observed for samples. The dielectric behavior gave information on the re-orientation motions of dipoles and the conduction behavior of extrinsic ions in the samples.

Fig. 2.4 Programmable automatic RCL meter [FLUKE PM6306] used for dielectric studies.

Chapter 3

Results and Discussion

Dielectric spectroscopy of a number of FLC has been investigated and possible information about their molecular orientation and the relaxation process explained in detail [33-41]. It is due to the fact that these materials are very interesting and promising for practical applications [41, 42]. The dielectric measurements of Barium Ferrite Nano Particles and CNTs dispersed in SCE13 gives useful information about the properties of these compounds. The ferroelectric

Morphological Studies of Barium Ferrite Nano Particles and CNT dispersed SCE13

Mechanical agitation was necessary to disintegrate such large agglomerates, but it alone was inadequate to achieve finer dispersion. We therefore employed sonication to the nano particles-SCE13 mixtures for about 2 hours. Figure shows micrographs of 0.05% and 0.075% dispersed Barium Ferrite Nano Particles and CNT obtained under crossed polarizers at an elevated temperature appreciably above the smectic– isotropic transition temperature in FLC.

10X

10X

Fig3.1 represents various phases in SCE13 dispersed Barium Ferrite Nano Particles having concentration of 0.075%

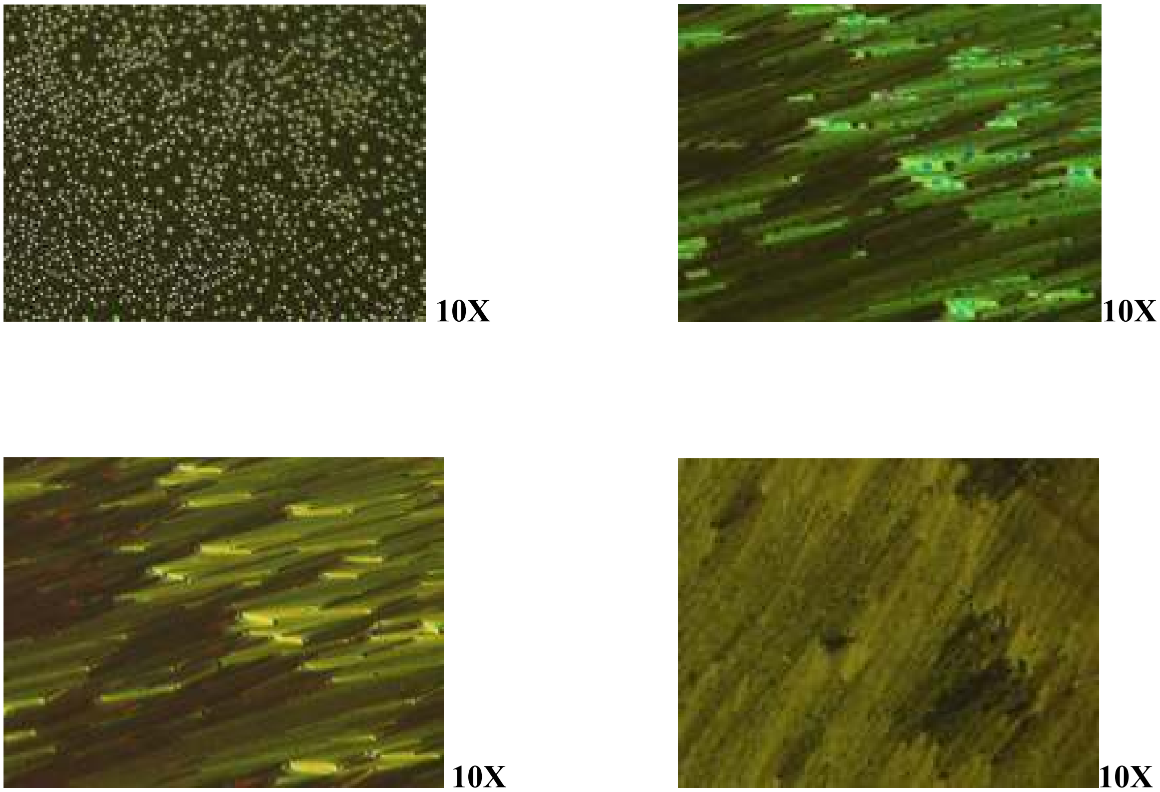


Fig3.2 represents various phases in SCE13 dispersed CNTs having concentration of 0.075%

Dielectric spectroscopy

Temperature dependence of dielectric permittivity (ε')

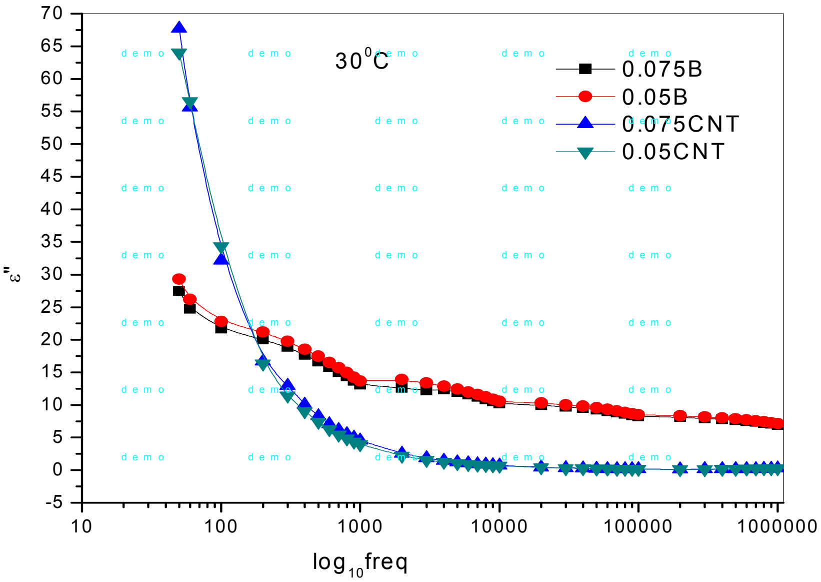
The temperature dependence of dielectric permittivity ε' at different frequencies is shown in Figure below. The trend is same at low and even at higher frequencies. It means that this composite mixture can be used at low as well as higher frequencies. But the value of dielectric permittivity decreases with temperature because the thermal agitation become more dominant over intermolecular interactions which results in collisions between molecules and hence randomization of dipoles. This randomization results in decreased dielectric permittivity at higher frequencies.

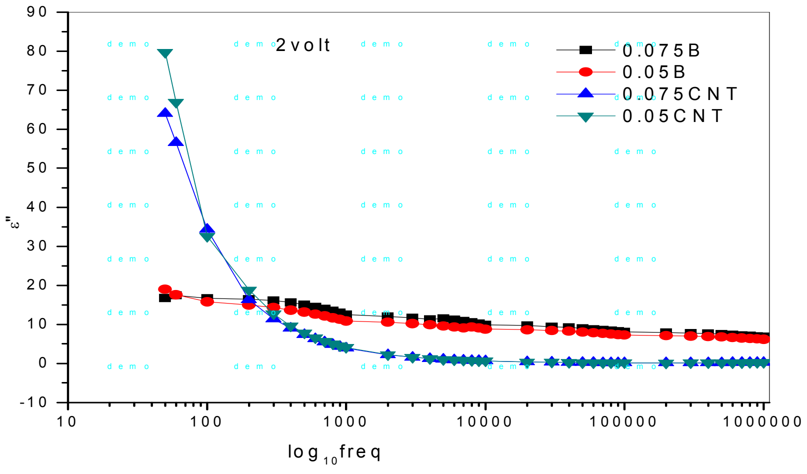
From graphs 3(a), 3(b) it is clear that at a constant frequency of 50 Hz , if we compare the values of permittivity vs temperature, we observe that while dispersing Barium Ferrite nano particles, the value of permittivity shoots to 18 at a concentration of 0.075% and it is 16 at a lower concentration of 0.05%. If the same concentration is compared to CNT then its value is lower and is 13 and 12 respectively. While at higher temperatures, there is no significant change. Also even at higher frequencies, there is no significant change in the value of permittivity. This is due to the reason that at higher frequencies, the molecules do not have enough time to orient in the direction of field. The permittivity values obtained on dispersing Barium Ferrite nano particles is more than dispersing CNTs in the same material. This can be obtained on the basis of shape of nano particles. The liquid crystal we are using is rod like. CNTs are also rod like and Barium Ferrite nano particles are spherical in shape. When we disperse Barium Ferrite nano particles, they disperse very easily on the rod-shaped molecules while CNTs itself are rod like and the alignment of these rods with the liquid crystal rods is not very easy and sometimes we have to apply electric field and hence the values of permittivity is lower.

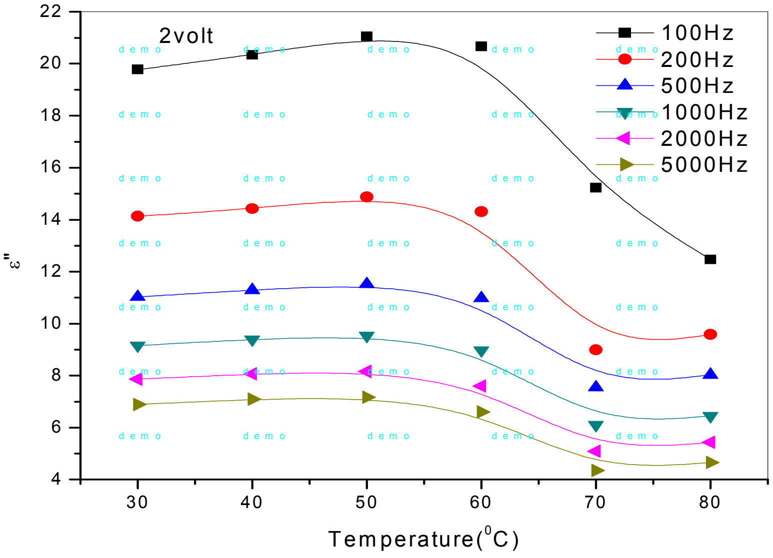
Frequency dependence of dielectric permittivity and dielectric loss (ε', ε '')

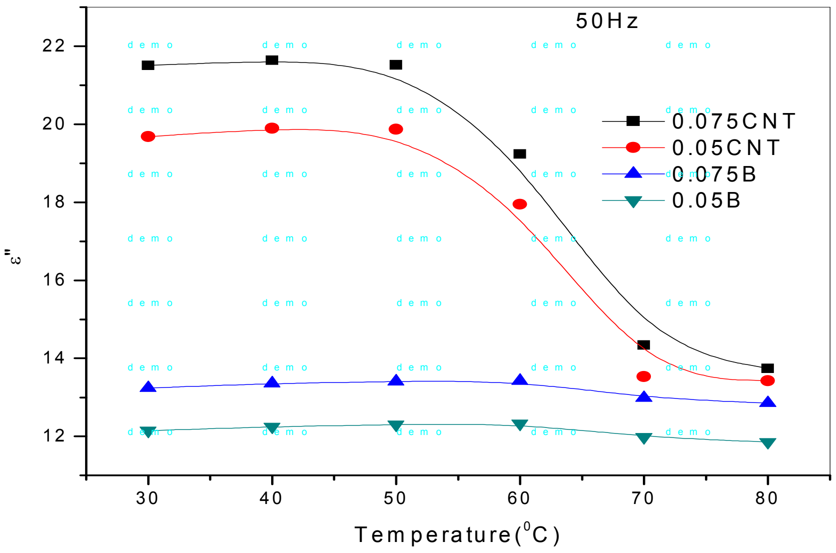
Fig shows the effect of frequency on dielectric permittivity at different temperatures.

The permittivity decreased exponentially up to a frequency of ~1 kHz at all temperatures. At higher frequencies dipoles do not show simultaneous response to electric field and hence they do not align along the field direction. Thus dielectric permittivity is decreasing. From graphs 3(c), 3(d) it is clear that at a particular temperature of 30^{0}C, if we compare the values of permittivity vs frequency, we observe that while dispersing Barium Ferrite nano particles, the value of permittivity shoots to 20 at a concentration of 0.075% and it is 16 at a lower concentration of 0.05%. If the same concentration is compared to CNT then its value is lower and is 14 and 10 respectively. While at higher temperatures, there is no significant change.




2volt
0.075B
0.05B
0.075CNT
0.05CNT
ε''
90
80
70
60
50
40
30
20
10
0
-10
10
100
1000
10000
100000
1000000
$\log_{10}$freq


2volt
100Hz
200Hz
500Hz
1000Hz
2000Hz
5000Hz
ε''
22
20
18
16
14
12
10
8
6
4
30
40
50
60
70
80
Temperature(^{0}C)



CHAPTER 4

Conclusions

- Our results indicate that adding a low concentration of nano particles (CNT+ barium ferrite) into a ferroelectric liquid crystal matrix to form composites, have attracted much attention because of their unique morphological and dielectric properties. The ferroelectric liquid crystal ordering makes it difficult to suspend small nanotubes in a liquid crystal host. Nanotubes often segregate into agglomerates distributed non-uniformly in the cell. The resulting spatial distribution of the nanotubes is difficult to control. While the distribution of Barium Ferrite nano particles is homogeneous.
- Dielectric permittivity increases with the addition of Barium Ferrite nano particles in comparison to CNTs at lower frequencies, while at higher frequencies there is no significant variation. Also at higher temperatures, dielectric permittivity decreases.
- Dielectric loss decreases with the addition of Barium Ferrite nano particles in comparison to CNTs at lower frequencies. Even at higher frequencies, it is noted that losses are decreasing. So, this composite material can be used for high frequency applications.

- Overall it can be concluded that with the addition of nano particles, permittivity decreases to a greater extent. But this can be compensated with dielectric losses. So this composite material can be used for high frequency applications.

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