Preface

Liquid Crystal (LC) represents intermediate state of matter, which is identified for its properties of crystalline solids and as well as liquids. Since its discovery in biological systems by Reinitizer in 1888, the field of LCs has grown enormously in specific areas for applications in display devices. For exhibiting both fluid and crystalline properties in LC phase the materials are utilized in many applications and modern appliances such as thermography, Electro-Optic displays, and medical diagnostic tools. Now a days the largely used Flat Panel Displays are of such kind of optoelectronic devices. Many technologies and different materials are running towards the preparation of effective flat panel displays [1] and material science research can play a decisive role in it. Amongst them “Liquid Crystals” play a major role in the preparation of Flat Panel Devices.

Measurement of dielectric properties in a wide frequency range can provide information on the conduction mechanism, interfacial polarization and molecular dynamics. Dielectric constant is a characteristic property of a material and it has contributions over to the orientational polarization, space charge polarization, dipolar polarization, ionic polarization and electronic polarizability which are functions of frequency and temperature. The present work thus involves low frequency dielectric studies on different mesogens of Hetro cyclic, Fe₃O₄ nano doped and Ferro electric liquid Crystals. The temperature and frequency dependence of Capacitance C, Resistance R, Inductance L were measured by using Newton’s 4th Ltd., LCR meter model. The frequency range of measurement is from 1 Hz to 1 MHz and using this data calculated the different dielectric parameters. The accuracy of dielectric constant and loss were estimated to the extent of error margin 1% and 2% respectively and the temperature accuracy to ± 0.1°C.

Chapter 1: Introduction

This chapter contains general introduction regarding applications of LC materials in different phases. Their structural classification and chemical constitution are described. Literature collected in the field of dielectric studies on liquid crystalline materials is
presented and discussed in this chapter. The statement of the problem for doctoral work is appended at the end of this Chapter.

**Chapter 2: Experimental**

This chapter explains about the experimental techniques and their pictures, used for the characterization of selected samples, their derivatives, the preparation for samples of liquid crystals, main theories of dielectric and thermodynamic parameters. The basic concepts for the determination of dielectric permittivity ($\varepsilon'$), dielectric loss ($\varepsilon''$), molecular dielectric relaxation ($\tau$), conductivity ($\sigma$) relaxation frequency ($f_R$), activation energy ($E_a$) in liquid crystalline materials are presented in this chapter. The theoretical treatment on dielectric relaxation methods namely the Debye model, Cole-Cole model, Cole-Davidson model and Havriliak - Negami model, is also discussed in this chapter.

**Chapter 3 is divided in to two parts 3A and 3B.**

**Chapter 3A: Benzothiazole - based liquid crystals**

Interest in the study of mesomorphic heterocycles has dramatically increased in the recent years due to their wider range of structural templates as well as their optical and photochemical properties [2]. The significance of the heterocyclic core in determining the properties of liquid crystals have been reported in a series of review papers [3]. Heterocyclic liquid crystals can be synthesized for getting high dielectric biaxiality which is built in the compact core unit that considered as essential technological devices. These materials possess potential applications in spatial light modulation, all-optical signal processing, optical information storage, organic thin-film transistors, fast switching ferroelectric materials, fluorescent probes for the detection and analysis of biomolecules. The phase transition temperatures and textural changes in two homologous series of 2-(4- $n$ alkanoyloxy benzylidenamino) benzothiazoles (where $n$=12 and 16) were measured by using Meopta Polarising Optical Microscope are included in this chapter. Thermal microscopic studies used for confirming the occurrence of Smectic A phase in the materials. At high frequency both compounds exhibits almost constant $\varepsilon'$ showing lower values generally being associated with the lowest electrical loss characteristics. Due to the high orientation of liquid crystal molecules in isotropic phase
shows high value of $\varepsilon^1$ when compared with other phase. At lower frequencies the grain boundaries are more effective for conductivity and permittivity than grains. Therefore, permittivity is high at lower frequencies and decreasing as frequency increases. The decrease in permittivity takes place when the jumping frequency of electric charge carriers cannot follow the alternation of the applied a.c. electric field beyond a certain critical frequency. The data of Dielectric loss clearly show that low frequency data are affected due to ionic conductance, where as high frequency data effected by ITO resistance. As usual relaxation frequencies are seen to have shifted towards lower side with decrease in temperature.


Chapter-3B: Schiff Based Benzothiazole Core Liquid Crystals

Heterocyclic mesogens are usually incorporated with heteroatoms, such as N, O and S, resulting in a reduced symmetry in the overall molecule as well as the generation of a stronger polar induction. The inclusion of the heteroatom can considerably change the polarity, polarizability and to a certain extent the geometry of a molecule, thus influencing the type of mesophase, the phase transition temperatures, dielectric constants and other properties of the mesogens [4]. Examples of liquid crystals with incorporated heterocyclic rings are pyridine [1], thiophene [5], oxadiazole and benzoazole The phase transition temperatures and textural changes in homologous series of 6-methoxy-2-(4- n- alkanoyloxybenzylidenamino) benzothiazoles mesogens (n MBABTH) for n=14 and 16) are studied have using polarizing optical microscope. The temperature and frequency dependence of dielectric constant and dielectric loss are carried out in the frequency range from 1Hz to 1MHz. Changes in dielectric constant and loss are observed at low frequencies temperature dependence of activation energy and relaxation frequency studies was made for smectic and nematic phases. The intermolecular forces in Molecules for forming nematic mesophase are responsible for mutual parallelism in the molecular long axes resulted in a long-range order. The low loss frequency reflects cooperative nature of molecular orientation. The dielectric study reveals that these
compounds are useful for applications involving electro optic devices. The activation energy has showed similar tendencies in both samples as it is increased with increasing temperature. This effect is due to the role of the surface activity of dispersed particles on local order of the liquid crystal as a result of elastic distortions associated with the liquid crystal molecules.

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Chapter 4: Fe$_3$O$_4$ Nano Doped Liquid Crystals

Liquid crystals are very sensitive materials, changing their properties very quickly due to application of thermal stress, mechanical stress, electric and magnetic fields, by the process of doping impurities like non-liquid crystals, and liquid crystals and also nanomaterials. It is a well known fact that the properties of materials change as their size approaches to nano scale and the percentage of atoms at the surface of a material becoming significant. The unexpected properties of nano particles are therefore largely due the large surface area of the material, which dominates the contributions made by the small bulk of the material. The doping of various nano particles in a variety of materials finds extra – ordinary results. These find applications in biomedicine [6], bio-analysis [7], can alter significantly electronic, mechanical and chemical properties of base material [8]. However, presence of nano particles has an adverse effect on the growth and life of a plant. Dispersion of nano particles in industrial coatings to protect wood, plastics and textiles from exposure of UV rays is appreciable. This chapter explains phase transition temperatures and textural changes for thermotropic pure and nano doped p-n-alkyloxybenzoic acid mesogens studied at considerable time periods in order to observe the stability. Frequency and temperature dependent dielectric constant and dielectric loss for the pure and nano liquid crystals were carried out. The UV-Visible spectral study confirms the presence of Fe$_3$O$_4$ nano particles in the prepared nanodoped mesogens. At high frequency both the compounds exhibits constant $\varepsilon'$ and also shows lower values these are associated with the lowest electrical loss characteristics. The high orientation of liquid crystal molecules in isotropic phase shows high value of $\varepsilon'$ when compared with
other phase. On doping nano particles the strong anchoring forces developed among nano particles and liquid crystal molecules caused for decrease in dielectric permittivity. Fixed orientations of molecules have brought low values in liquid crystalline phase The conductivity has increased with the increased frequency of 1MHz. The maximum conductivity values studied at 1 MHz are $1.25 \times 10^{-4}$ (S/m) in isotropic state for nano doped LCs N3OBA and $1.07 \times 10^{-4}$ (S/m) for 3OBA. Having the lowest carbon chain length in the series the mobility of molecular rotation in 3OBA has led to increase in flow of current in anisotropic LCs matrix than in other compounds upon their gradual increased chain lengths in the series. In the observed frequency range, the temperature dependent dielectric constant stability (temperature coefficient of dielectric constant,$\tau_e$) had shown frequency shift thermotropic liquid crystals, corresponding to the change in the dielectric constant values is observed.

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**Chapter 5: Ferroelectric liquid crystals**

Chiral compounds are able to form liquid crystals with structures similar in way of those of non-chiral materials but with different properties. The cholesteric (or twisted chiral nematic) and blue phases are related to non-ferroelectric and the chiral smectic phases exhibiting ferroelectric properties. The chiral smectic phases due to their low symmetry are able to exhibit spontaneous polarization and piezoelectric properties. In the chiral nematic phase the director varies in direction throughout medium in a regular way and displays a continuous twist along the optic axis leading to a helical structure. Due to the twisted or helical structure, the $N_t$ phase possesses special optical properties, which make it very useful in practical applications. This chapter presents the study made for the phase transition temperatures, textural changes and Low frequency dielectric relaxation, studies are carried out on a ferroelectric liquid crystal compound $(S)$-(-)-2-Methylbutyl4'-(4'-$n$-alkanoyloxybenzoyloxy) biphenyl-4-carboxylates (S-MB-$n$B-BC) where $n$=16 and18, exhibiting Smectic C* and Smectic-A. The dielectric loss spectrum has observed that there is a cross over
frequency in both the compounds. Dipolar relaxation SmecticC* and Smectic A, phases is found to follow Arrhinius shift through their activation energies. The Cole-Cole plots are found to yield an increasing $\alpha$ values with the decreasing temperature for all the phases in both the compounds. With the decrease of temperature, $\alpha$ value increases upon relatively confined frame of the dipole. It is also noticed that the observed increasing dielectric increment $\Delta \varepsilon$ with the decreasing temperature has been effectively influenced by the low frequency end of dispersion during LF mechanisms that are exhibited by all phases in the both compounds. This trend of relative permittivity $\varepsilon_r$ being more susceptible to lower frequency dielectric field infers the characteristic liquid crystalline response more pronounced at lower frequencies.

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**Chapter 6: Summary and Future scope**

This chapter summarizes the results of work carried out and presents important findings along with future scope of the work.