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Behaviour of Dielectric properties of Liquid Crystal Mixture Doped with Ferroelectric Nanopowder

Rita A Gharde[1], Sangeeta Y.Thakare[2]

[1, 2]Department of Physics, University of Mumbai, Mumbai

Abstract: ***In this paper we present the results based on electro-optical and dielectric properties of Liquid Crystal (LC) mixtures, doped with ferroelectric nanoparticals(NPs) SrTiO3 in the concentration of 0.1wt %,0.3wt % and 0.5wt % of NPs. Nanoparticles (NPs) have emerged as extremely promising materials to alter and improve the properties of Liquid crystals (LCs).It is observed that the clearing temperature of doped LC mixture is increased with increase in concentration of NPs. The electric field induced by polarized nanoparticles enhances the orientation coupling in a LC mixture results in increase of clearing temperature. The mixture of liquid crystals influences the molecular orientation of liquid crystal compound consequently affecting their physical properties .we have observed the dielectric constant ,dielectric loss factor and electrical conductivity of all the samples as a function of temperature . We found the phase transition temperatures of all the samples by Fabery Perot Spectroscopy (FPSS), and Differential Thermal analysis (DTA). The textures of different mesophases of the samples are recorded by using Optical Polarizing microscopy (OPM). The LC mixtures show phase transition temperatures and other physical properties which are different from their constituents. Doping of LC mixture with 0.5 % wt of NPs concentration has improved the optical and electrical and dialectical properties of the LC mixture.***

Keywords: ferroelectric liquid crystal, Nanoparticles , Fabery Perot Spectroscopy (FPSS), Differential Thermal analysis (DTA). Optical Polarizing microscopy (OPM

1. Introduction

Liquid crystals (LCs) have received much attention in the recent years because of their ability to transfer their long range orientational order on the dispersed materials, such as carbon nano-tubes, nano-particles and various collides [1]. The importance of liquid crystal is increasing constantly due to their wide spread use in display technology and other devices .For application of any liquid crystal in a practical device, it must retain suitable values of certain parameters like dielectric permittivity, dielectric loss, conductivity, refractive index, birefringence etc. with varying conditions like temperature and electric field .To achieve this , Usually liquid crystal mixtures are used which has important role in device applications. Liquid Crystals mixtures show phase transition temperatures and other physical properties which are different from their constituents. Many researchers are trying to improve the dielectric and electro-optical performance of LCDs by doping them with non-mesogenic material, such as polymer, dye, nano-particle, carbon nano-tubes . It is found that the doping of nanoparticles has improved the electro-optical characteristics of various display devices.[3–5] .Initially Doping of nanoparticles was restricted to Nematic Liquid Crystals(NLC) due to their widespread applications, and relatively simple liquid crystal structure . Doped NLC showed the enhancement of the electro-optical properties of NLC. After that cholesteric liquid crystal and smectic liquid crystal are used for doping of NPs. Doped cholesteric liquid crystals, showed improvements in the contrast of reflectance of planar-focal conic state, and driving voltage of the cholesteric liquid crystal .Ferroelectric liquid crystals (FLCs) have been explored for fast switching and memory devices. The FLCs have become a very attractive material for research due to its helical structure and chirality of the molecules. Spontaneous polarization and ferroelectricity Because of this they show faster response time and are beneficial for application in different fields. Enhancement of the electro-optical properties of liquid crystal is dependent on the size, type, concentration, and intrinsic characteristics of the nanoparticles used for doping. The nanoparticles should share similar attributes to the liquid crystal molecules and its size should not significantly disrupt the order of the liquid crystal. In this paper we used the mixture of Ferroelectric liquid crystal(FLC) and cholesteric liquid crystals(CLC). We doped this mixture with ferroelectric nanoparticals and observed the enhancement in opto-electrical and dielectric properties of LC mixture.

2. Materials

We have taken the mixtures of Cholesteric Nonanoate and 4-4’-n hexylphenyl benzoic acid (H0711) in the proportion of 90:10. Both are obtained from Sigma Aldrich and Merck respectively. The mixtures were prepared by weighing the components accurately with the help of an electronic balance. Then the liquid crystals were mixed by melting them together in a fusion tube to obtain homogeneous mixture. The mixture then cooled down to obtain solid which was grounded. We used ferroelectric nanopowder of Strontium titanate (SrTiO3) as a doping agent .SrTiO3 was mixed with oleic acid and heptane in appropriate proportion by weight and then mixed with liquid crystal mixture by ultrasonication method. The nanoparticles are doped into liquid crystals mixture in the concentration of 0.1% wt 0.3% wt and 0.5% wt.

3. Experimental Techniques

Optical Polarizing Microscopy (OPM)

OPM is used to characterize the textures of Liquid Crystals. From these textures we have analyzed the transition temperatures as well as nature exhibited by Liquid Crystals. The phase transition of liquid crystal between various mesomorphic forms occurs at a thermodynamically defined temperature as the liquid crystal undergoes a change in internal order at the point of phase transition.

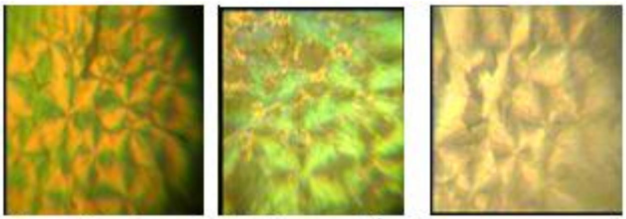
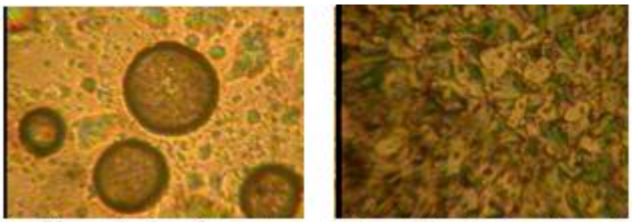

Crystalline phase at 40^{0}c Blue Phase at 90^{0}c cholesteric phase (N*) at 92^{0}C

Figure 1.1: Textures of Cholesteryl Nonanoate

Cholesteryl Nonanoate exhibits a monotropic smectic (SmA) phase with chiral nematic or cholesteric (N*) and blue phase in the cooling cycle. Its clearing temperature is 94^{0}C.When it is cooled from isotropic phase, chiral nematic phase appered at 92^{0}C ,blue phase at 90^{0}C and at focal conic smectic A at 76 ^{0}C .It crystallizes at 40$^{\mathbf{0}}$C**.**

In N* phase, in addition to the long range orientational order there is a spatial variation of the director leading to a helical structure. The local preferred direction of alignment of the molecules is slightly rotated in adjacent planes perpendicular to the pitch axis. The helical pitch in the N* phase is substantially larger than molecular dimensions and varies with the molecules.

Textures of H0711-


Nematic droplets at clearing point 222^{0}c Focal Conic Fan-shaped texture180^{0}c

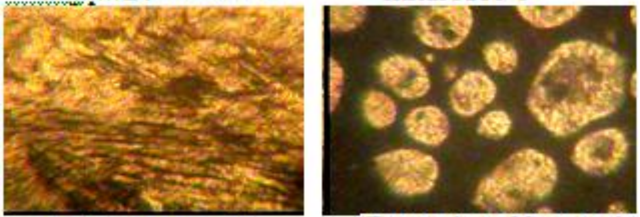

SmC* texture with helix lines a 118 Formation of S_G mosaic texture 95 ^{0}c

Figure 1.2: Textures of H0711

The isotropic temperature of H0711 is 225^{0}c. When cooled from isotropic phase , nematic phase appeared at 222^{0}c, Upon further cooling SmAFan-shaped texture appears at 180^{0}c,whichg turn into SmC* texture at 118^{0}c. At 95^{0}c, S_G mosaic texture is observed.

The chiral smectic C (SmC*) liquid crystalline phase, has a helical stack of layers in which molecules are uniformly tilted. The tilt of the molecules is coupled to the layer thickness producing local biaxiality in the medium. Due to the chirality of the molecules, the mirror symmetry in the system leads to the possibility of sustaining an electric polarization (P), along the local twofold axis, spiraling uniformly about the twist axis of the helical structure

Textures of Ch.Nonanoate+H0711-.

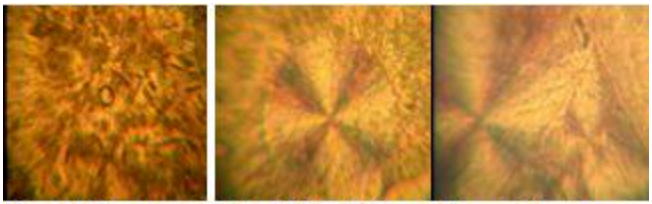

Nematic Texture at 104^{0}c Focal Conic Fan Texture at44^{0}c Recrystallization at 41^{0}c

Figure 1.3: Textures of H0711+Ch. Nonanoate

The isotropic temperature of the LC mixture is 117 ^{0}c which is much lower than pure FLC. The sample melts at 76 ^{0}c. During cooling cycle the Nematic texture observed at 104 ^{0}c . The growth of SmA batonnets from the isotropic melt has started at 44 $^{\mathbf{0}}$**c** . The sample crystallizes at 41^{0}c . It indicates that the smectic A phase stability is reduced and lower than that of the pure LCs. The mixture has stabilized and broadens the temperature range of the Nematic phase than in Ch.Nonanoate. The LC mixture has disrupted the molecular packing which has reduced melting point and also smectic phase stability.

Textures of H071+Ch.Nonaoate+0.1% wt of NPs-


Schelerian Nematic at 135 ^{0}c Focal Conic Fan Shaped Texture at 41^{0}c Rerystallization at35^{0}c

Figure 1.4: Textures of H071+Ch.Nonaoate+0.1% wt of NPs

Doping of 0.1%wt of NPs in the binary mixture has increased the isotropic temperature to 140 ^{0}c .When cooling from isotropic state, Nematic texture is observed at 135^{0}c .Focal Conic Fan shaped Sm A texture is appeared at 41 ^{0}c .Crystallization occurred at 35 ^{0}c . Addition of NPs also improved the stability of the N* phase. The smectice phase stability is reduced by 26 ^{0}c and the isotropic temperature is increased by 23 0c than the LC mixture isotropic temperature. The Melting temperature of the sample is 71^{0}c. NPs in the mixture has reduced the melting temperature of the sample by 5^{0}c .

Textures of H071+Ch.Nonaoate+0.3% wt of NPs

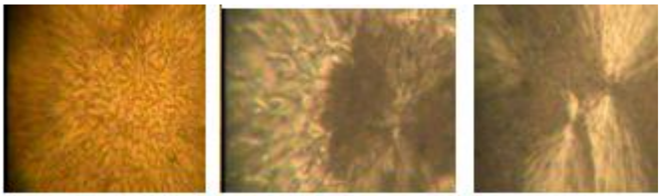
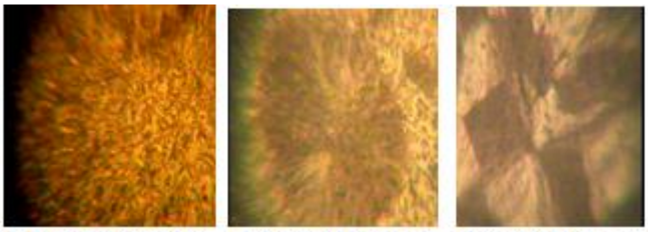

Schelerian Nematic at 140^{0}c Focal Conic Fan shaped at 45^{0}c Recrystallization at 36^{0}c

Figure 1.5: Textures of H071+Ch.Nonaoate+0.3% wt of NPs

The isotropic temperature of LC mixture with 0.3%wt of NPs is 145 ^{0}c .The melting temperature of the sample is 70 ^{0}c which is decreased by 6 ^{0}c than the LC mixture melting temperature. When cooling from isotropic state, chiral Nematic texture is observed at 140^{0}c.Focal Conic Fan shaped Sm A texture is appeared at 45 ^{0}c . The sample crystallizes at at 36 ^{0}c .The smectice phase stability is reduced by 27 ^{0}c than the LC mixture. The isotropic temperature is increased by 28 ^{0}c.

Textures of H071+Ch.Nonaoate+0.5% wt of NPs



Schelerian Nematic phase at 150 ^{0}c

Focal conic Sm A phase at 55^{0}c

Rerystallization at 50^{0}c

Figure 1.6: Textures of H071+Ch.Nonaoate+0.5% wt of NPs

Doping of 0.5%wt concentration of NPs in the binary mixture has clearing temperature 152^{0}c, which is increased by 35^{0}c compare to LC mixture. When it is cooled from isotropic state, Schelerian nematic texture obtained at 150^{0}c Focal conic phase appeared at 55^{0}c .The sample crystallizes at 50^{0}c .the melting temperature of the sample is 73^{0}c which is less by 3 ^{0}c than the LC mixture. The smectic phase stability is reduced by 24^{0}c.The LC mixture doesn't exhibit ferroelectric phase. This is because the steric hindrance suppresses the ferroelectric phase.

3.1 Fabery Perot Scattering Spectroscopy (FPSS)

FPSS is the optical technique of measuring the diameter of Fabery-Perot rings obtained from Fabery-Perot interferometer coupled with a spectrometer. It has been used to determine the phase transition temperatures (PTTs) of liquid crystals.

Table 1: Phase Transition Temperatures by FPSS

H0711	80,90,115,165,188,200,225
Chl.Nonanoate +H0711	41,56,69,86,93,125
Ch.Nonanoate +H0711+0.1% STrio3	40,55,76,90,105,121,135,140
Ch.Nonanoate +H0711+0.3% STrio3	53,60,83,90,102,123,137,145
Ch.Nonanoate +H0711+0.5 % STrio3	60,80,110,115,130,140,152

Differential Thermal Analysis (DTA)

The phase transition temperature of liquid crystals can be obtained from DTA curve. It involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference. The DTA thermograms showing the variations of the heat flow (mW) with temperature (°C) at a scan rate of 5ºC/min in the heating and cooling cycles of all the samples are shown here.

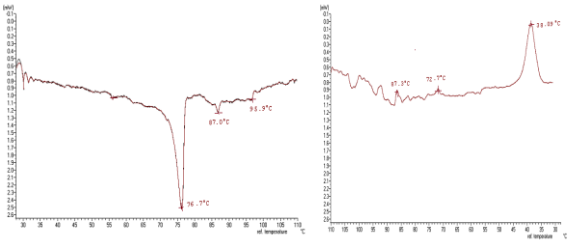


Figure 1.13: DTA thermogram of Ch.Nonaoate

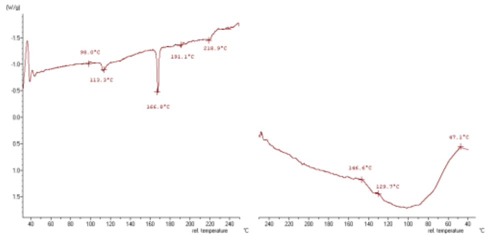


Figure 1.14: DTA thermogram of H0711

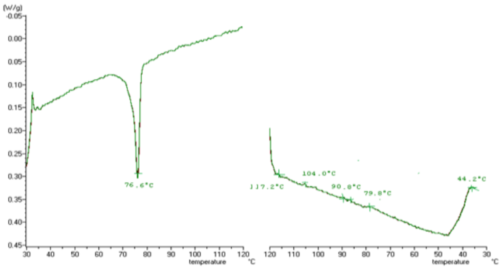


Figure 1.15: DTA thermogram of Mixture

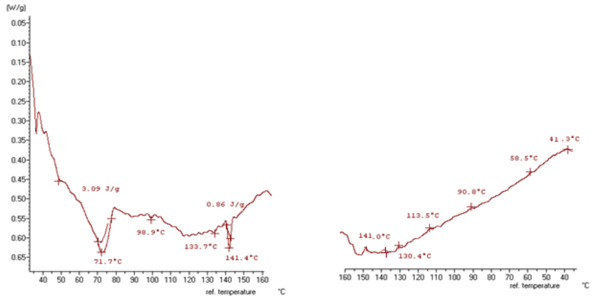


Figure 1.16: DTA thermogram mixture+0.1wt NPs

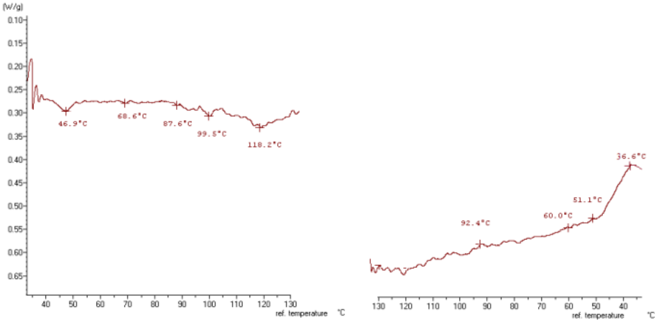


Figure 1.17: DTA thermogram of mixture+0.3wt NPs

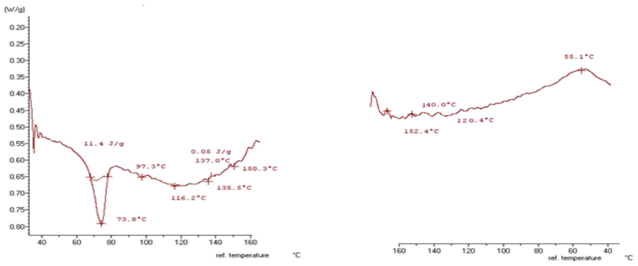


Figure 1.18: DTA thermogram of mixture+0.5wt NPs

Table 2: Phase Transition Temperatures by DTA

Sample	Phase transition Temperature
Ch.Nonanoate	38, 72.1, 76.7,87,95
H0711	47,98,113.3, 129.7, 146.6,166.8,191,218
Chl.Nonanoate +H0711	44.2,76.6, 79.8, 90.8, 104.2,117.2,
Ch.Nonanoate +H0711+0.1% STrio3	41.3,58,71.7,90,98.9,116,113, 130,133,141,148
Ch.Nonanoate +H0711+0.3% STrio3	36.6,46.9, 51.1,68.6,87.6,99.5,118.2,145
Ch.Nonanoate +H0711+0.5 % STrio3	55,73.8,97.3,116.2, 120, 135,135, 140, 150, 152,

The DTA graphs show a broadening of the peaks as we increase dopant concentration. The peak broadening is not due to phase separation of the mixtures. The broadening is exhibited for all transition peaks between phases. The peak broadening indicates that the LC molecules are hindering transitions between the phases, as the mixtures are taking longer time for a complete rearrangement of the molecules.

UV-VIS Spectroscopy

A UV-Vis spectrophotometer measures the amount of light absorbed at each wavelength of the UV and visible regions of the electromagnetic spectrum. Absorption of radiation by a sample is measured at various wavelengths and plotted by a recorder to give the spectrum which is a plot of the wavelength of the entire region versus the absorption (A) of light at each wavelength. The absorbance depends on the electronic structure of the compound and also upon the concentration of the sample and the length of the sample cell. Absorption of infrared radiation by a molecule leads to increased vibrations of covalent bonds electrons are promoted from low-energy ground state or orbitals to higher-energy excited-state orbital. The wavelength of UV or visible light absorbed depends on the ease of electron promotion. Molecules that require more energy for electron promotion absorb at shorter wavelengths. Compounds that absorb light in the visible region (that is colored compounds) have more-easily promoted electrons than compounds that absorb at shorter UV wavelengths.Fig1.19-1.22 show UV-Vis absorption spectra of all the sample.

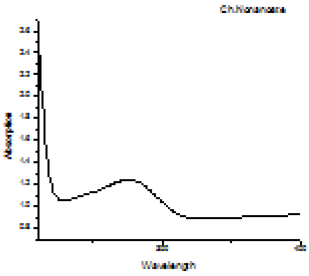


Figure 1.19

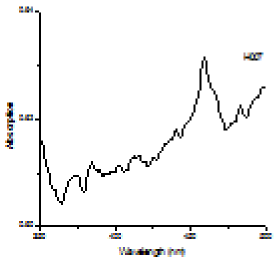


Figure 1.20

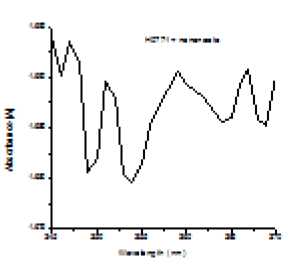


Figure 1.21

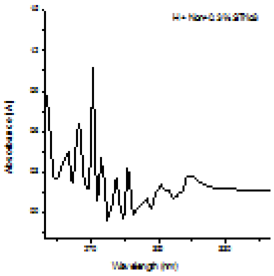


Figure 1.22

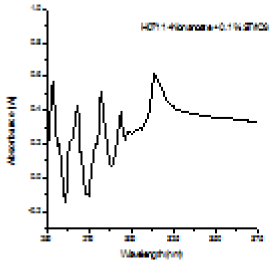


Figure 1.23

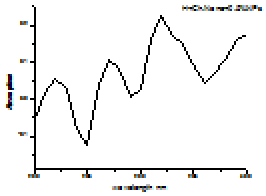


Figure 1.24

H0711 shows the maximum absorption at 457 nm, and which attributes to π→π* transition. It is primary absorption. And secondary absorption is observed at 300nm. Ch.Nonanoate at 273nm, which attributes to π→π* transition. Compounds whose molecules contain conjugated double bonds have absorption maxima at longer wavelengths.

Less energy is required to promote a π electron , this is because , the energy gap between the conjugated double bonds is less .Hence the compound absorbs UV radiation of longer wavelengths .Its mixture with Ch.Nonaoate shows absorption at longest wavelength at 230nm.But the intensities of absorption has been increased. With increase in concentration of NPs, the absorption intensities are increased. It also shows, increase in absorption of longer wavelengths with increase in NP concentrations.

Table 3: Maximu Absorption λmax in nm

Compounds	λmax nm
Ch.Nonanoate	273
H0711	457
Ho711+Ch.Nonanoate	230
Mixture+0.1% NPS	253
Mixture+0.3% NPS	265
Mixture+0.5% NPS	313

Raman Spectroscopy

The Raman scattering technique is a vibrational molecular spectroscopy which derives from an inelastic light scattering process. With Raman spectroscopy, a laser photon is scattered by a sample molecule and loses (or gains) energy during the process. The amount of energy lost is seen as a change in energy (wavelength) of the irradiating photon. This energy loss is characteristic for a particular bond in the molecule. Raman spectra of pure Liquid crystals, their mixtures and doped mixtures with NPs were examined by Raman spectrometer. A blue line at 488.0 nm of Ar+ laser was used as an excitation. All spectrums of all the compounds in powder form are observed at room temperature.

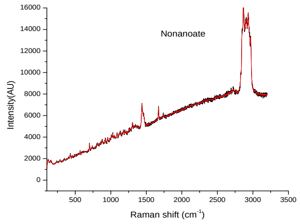


Figure 1.25 Raman spectra of Ch.Nonaoate

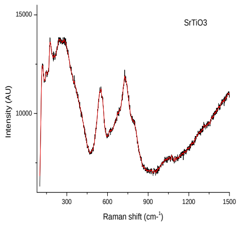


Figure 1.26 Raman Spectra of NP

The Raman spectrum of strontium titanate consists of seven Raman lines, one of which is of low frequency, 6 of these Raman lines have been interpreted as the first order spectrum arising from a small deviation of the cubic strontium titanate from its idealized symmetry. The four vibrational modes of the unit cell of $SrTiO_3$ correspond to frequencies of 100, 335, 441 and 620 cm^{-1} observed in Raman effect. The large width of the Raman lines and the additional lines at 256 cm^{-1} and 726 cm^{-1} have been attributed to a splitting of the longitudinal and transverse optical modes.

Cholesterytl Nonaoate shows strong band at 2850 cm^{-1} and - 2950 cm^{-1} which attributes to (C−H). Two medium bands are observed at 1440cm^{-1} which attributes to aromatic ringand 1680 cm^{-1} which attributes to C=O bond.

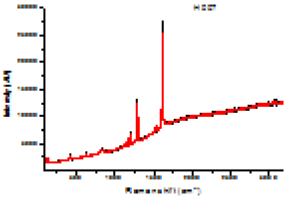


Figure 1.27 Raman Spectra of H0711

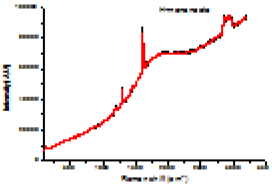


Figure 1.28 Raman Spectra of Mixture

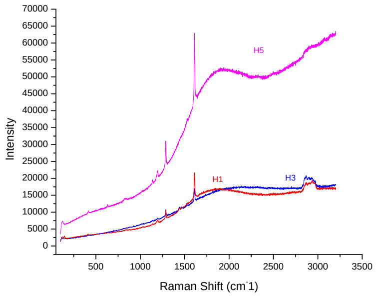


Figure 1.29: Raman Spectra of Doped Samples

The Raman spectra of H0711 contains the band lying between 700 cm−1 -1800 cm−1 .The intense bands at 1590 – 1600 cm−1 is assigned to the C-C stretching mode of the benzene ring. The band appears at 1239 – 1255 cm−1, which is connected with the aromatic ring vibration . The presence of a band at 1283 cm−1 related to the C-C stretching vibration of the aromatic ring. Its mixture with Ch.Nonaoate shows appearance of band at 2850 cm^{-1} and - 3100 cm^{-1} which attributes to (C−H). Though the positions of other band are same, the intensities of the bands are high than the pure LCs. With addition of NPs, the intensities are decreased than the intensities of bands in LCs mixture. With 0.5%wt concentration of NPs the band at 2850 cm^{-1} and - 3100 cm^{-1} are disappeared. The intensities are lowest in 0.3%wt concentration with slight increase in 0.5%wt concentration of NPS. Other band positions remain same.

Order Parameter

Order Parameters of all the samples are estimated from Haller's equation.

$$S = \left(\frac{T_c - T}{T_c}\right)^{\beta}$$

Where Tc is clearing temperature and β is constant, depends on the molecular structure and its value is close to 0.25.

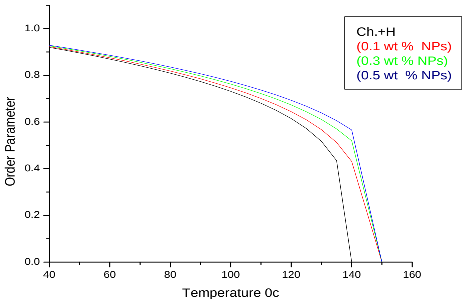


Fig 1.30 Order parameter of all samples

The order parameter S value of all the samples of different concentrations was estimated at different temperatures. It is observed that the order parameters of LC mixture are less than the pure LCs but more than order parameter of Ch. Nonaoate.It is due to that the mesogenic dopants can interact with LC molecules more strongly than the molecules with themselves and disrupt the orientational ordering of LC molecules .with addition of NPs in LC mixtures shows the order parameter S increases with increasing concentrations of NPs. Due to the large permanent dipole moments, ferroelectric nanoparticles induce realignment of neighboring liquid crystal molecules, thereby increasing the order parameter . There is less difference in order parameter with 0. 1% wt of NPs and the LC mixtures .It indicates that the influence of nanoparticals enhanced the molecular interaction in LC host. The variation of order parameter with temperature is dependent on the orientation order.

4. Conductivity Measurement

The conductivity and dielectric constant have been measured by Precision Impedance Analyzers, Model no.6500B which is highly accurate high frequency component analyzers. Figure 1.31- 1.36 show variation of conductivity of all samples with temperature.

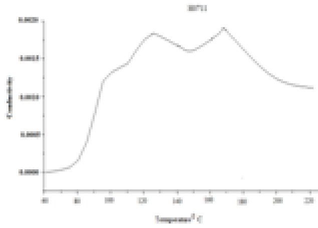


Figure 1.31

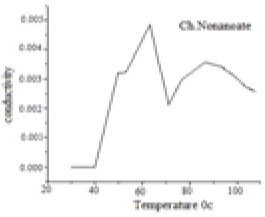


Figure 132

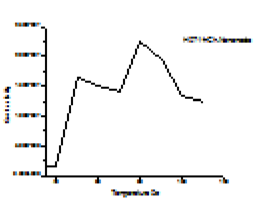


Figure 1.33

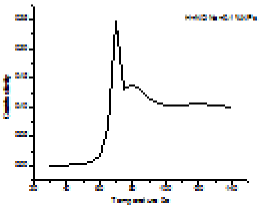
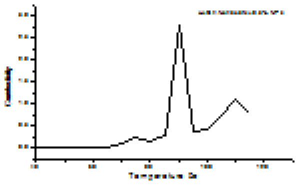


Figure 1.34



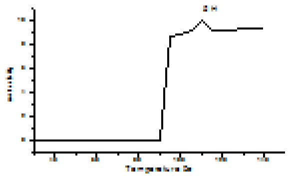


Figure 1.35 Figure 1.36

The conductivity increases with temperature and decreases towards isotropic temperature. The conductivity of the FLC increases with the increase in temperature and achieve its maximum value at SmC *phase transition temperature. The conductivity of the doped LC mixture increases with increase in concentration of NPs. This is because the ionic impurity of the LC mixture is reduced by nanoparticals. The conductivity of LC mixture with 0.5wt % of NPs is more than other concentrations.

5. Dielectric Constant Measurement

Effect of Temperature

The effect of temperature on dielectric constant is observed at the frequency of 100KHz.Fig 1.37-1.39 show variation of dielectric constant with temperature of all the samples.

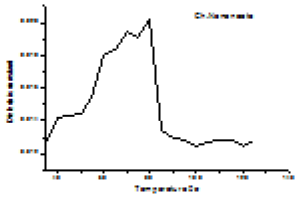


Figure 1.38

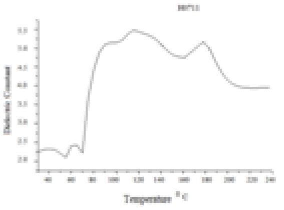


Figure 1.39

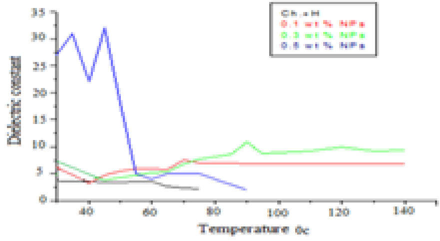


Figure 1.40

In each sample dielectric constant (ε′) values show discontinuities, indicating the phase transitions. For Ch.Nonanoate the value of ε′ increases with increase in temperature till it reaches cholesteric phase where it falls sharply. With further increase in temperature ε′ decreases until isotropic phase is obtained. For H0711, ε′ incrteses sharply from 70^{0}c,afterthat it shows variation at phase transitions. The value in SmC* phase at 118^{0}C is the more , which indicates the maximum helix strength in the FLC sample. It decreases near SmC* toSmA phase transition because helix starts unwinding. It again increases at 180 ^{0}C indicating phase transition .Further increment in temperature did not cause any appreciable change in the ε′ value, which implies that helix is completely unwound. The values of ε′ decrease with increase in temperature. In isotropic phase it remains constant. In isotropic phase, the variation in the value of ε′ is much small like normal liquids. The dielectric constant of LC mixture is higher than the pure LCs .The dielectric constant value is increased with increasing concentration of nano particals (NPs) in LC mixture. It is observed that 0.5% wt concentration of NPs in LC mixture has high value of ε′. the increase in the dielectric constant of doped mixture is caused by the permanent dipole moments and geometrical anisotropy of the ferroelectric nanoparticles.

Effect of Frequency

The frequency dependence of dielectric constant of all the samples at 35^{0}c are shown in following figures 1.41 -1.46

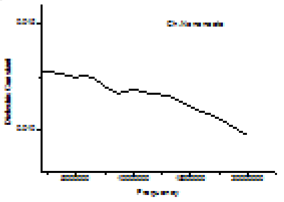


Figure 1.41

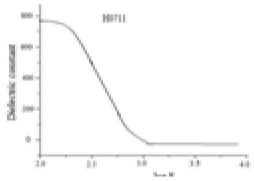


Figure 1.42

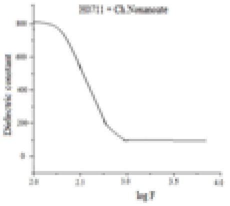


Figure 1.43

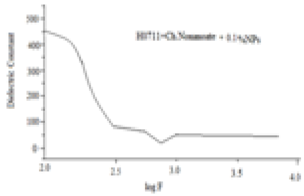


Figure 1.44

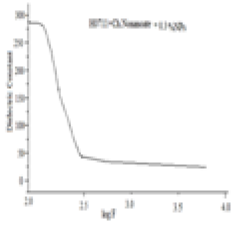


Figure 1.45

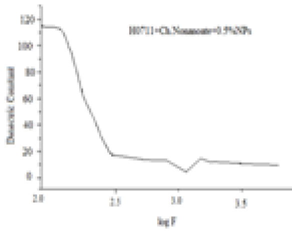


Figure 1.46

The value of dielectric constant increases at lower frequencies while it remains almost constant at higher frequencies. The decrease in ε’ with increase in frequency simply comes from the fact that polarization does not occur instantaneously with the application of electric field as charges possess inertia. Low frequency contributions are affected by electrode polarization, capacitance and ionic conductance whereas higher frequency effects are caused by ITO resistance and lead inductance. The presence of ions in FLC material can contribute largely to *ε’ in* the low-frequency regime resulting in the higher values of ε’.

The dielectric loss factor

The effect of temperature on dielectric losses at frequency 10KHz is shown in following Figures.1.47-1.52

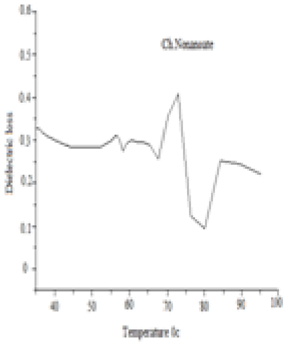


Figure 1.47

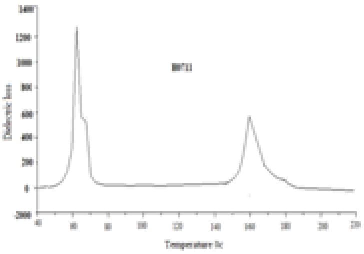
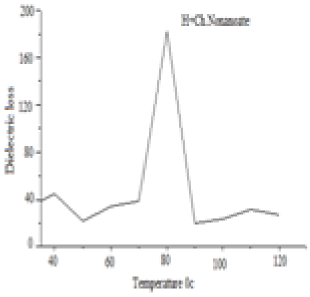


Figure 1.48



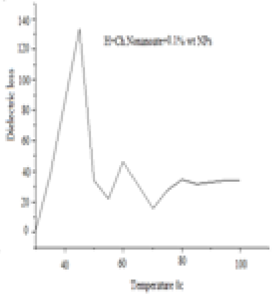


Figure 1.49 Figure 1.50

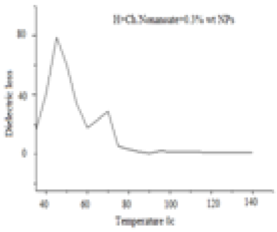


Figure 1.51

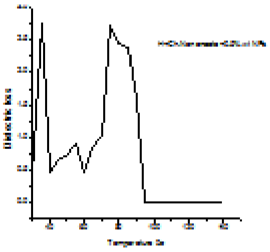


Figure 1.52

It has been observed that the dielectric loss shows variation with change in temperature. The LC mixture shows dielectric loss less than pure FLC. While the dielectric loss for all doped mixture is lower as compare to pure LCs. This proves that the NPs provide a more ordered LC system in which loss factor reduces .The dielectric loss is less in 0.5% wt concentration of NPs in LC mixture than other concentration.

Table 4: Values of Dielectric constant (ε') of all the compounds at 30^{0}c

Compounds	Dielectric constant
Ch.Nonanoate	0.01280
H0711	2.25
Ho711+Ch.Nonanoate	3.8
Mixture+0.1% NPS	6.21
Mixture+0.3% NPS	7.1
Mixture+0.3% NPS	27

6. Conclusion

We observed that low concentration of nanoparticle enhances the orientation coupling in a LC and leads to the increase of the clearing point. This increase is related to a permanent polarization of the ferroelectric nanoparticles. They have also improved the phase stability in LC mixtures. In UV-Vis absorption spectra the FLCs absorb the longer wavelength of light than the LC mixtures and doped mixtures. This is because of the Stabilizing effect of the pitch in the FLCs. The dielectric loss is less in doped LC mixtures compared to pure LCs and their mixtures. This loss is less in 0.5% wt of NPs in LC mixtures compare to other concentrations. The doped LC mixture show high value of conductivity compare to pure LCs and their mixture. This can be attributed to the reduction in ionic impurity by nanoparticals. The conductivity and dielectric constant of LC mixtures with +0.5 % wt of NPs is found to be high.

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Author Profile

Rita A. Gharde has obtained her Ph.D. degree in 2002 from University of Mumbai. Mumbai (India). Currently, she is an associate professor in the department of Physics, Mumbai University. Her field of interest in research is the study and characterization of the pure and doped liquid crystals. Sangeeta Y. Thakare is a research Scholar, pursuing her Ph.D. under the guidance of Rita A. Gharde. Her research is focused on the dielectric and electro-optical studies of the ferroelectric liquid crystals.