Characterization and Mesomorphic Behavior of Liquid Crystals Doped with Nano – Powder

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ABSTRACT
Combination of ferroelectric nano – powder and anisotropic liquid crystalline gives rise to exceptional physical properties unknown for solid state materials. The outstanding properties of ferroelectric doped liquid crystal being their macroscopic dipole, the preparation must assume the uniform alignment of the mesogen. By selecting suitable liquid crystals, phase structure and chemistry of macromolecular structure, these physical properties can be optimized for special applications like optical, electrical etc.

In this paper, dispersed low mass nano – powder in liquid crystal is studied by various techniques viz. Polarizing Microscopy Studies (PMS), Data Thermal Analysis (DTA), Fourier Transform Infrared (FTIR) Spectroscopy, Ultraviolet Visible (UV) Spectroscopy.

Keywords:
Cholesteric Liquid Crystal (CLC), Polarizing Microscopy Studies (PMS), Data Thermal Analysis (DTA), Fourier Transform Infrared (FTIR) Spectroscopy, Ultraviolet Visible (UV) Spectroscopy

1. INTRODUCTION
Liquid Crystals (LC) are soft condensed matter and now commonplace in display devices, light modulator, temperature sensor and optical communication networks. They have different phases like Nematic, Smectic and Cholesteric. Cholesteric Liquid Crystals (CLC) are innovative class of functional materials and have attracted great deal of attention due their various applications in electro – optics. Suspensions of various micro – or nano – particles to CLC have recently been the subject of renewed interest because they combine the fluidity and anisotropy of CLC with specific properties of particles [1-5]. For example, dispersed ferromagnetic particles greatly enhance the magnetic properties of liquid crystals. Large colloidal particles form defects in liquid crystal matrices, producing large director deformations. Ensembles of these particles and defects can form complex structures.

The ferroelectric nano – particle dispersed CLC have attracted attention due to their convenient preparation technique and enhanced physical properties. The ferroelectric nano – particles are so small that macroscopically homogenous structures are obtained i.e. the suspension appear similar to the pure LC with no readily apparent evidence of dissolved particles.

For enhancing the physical properties, a proper selection of nano – powder for CLC depend upon various factors such type, size, shape, preparation method, surfactant concentration and amount of doping material. Our research is inspired by many previous publications that describe the behaviour of CLC doped with nano – particles [6-14]. The ferroelectric colloids can increase the liquid crystal phase transition temperature, influencing their order parameter and thereby birefringence. The advantage of ferroelectric particles over other material is that they significantly maintain the intrinsic properties of the material from which they are made and do not significantly perturb the director field.

In the present paper, we are discussing the report of the results which shows that the phenomenon due to general properties of LC suspension containing ferro – colloidal nano – particles made for Characterization and mesomorphic behavior of liquid crystals doped with nano – powder.

It is found that by dispersing ferroelectric nano – powder in CLC, transition temperature changes, formation of new functional group occurs and other changes in physical properties were found due to strong interaction between CLC and ferroelectric nano – powder.

2. MATERIALS AND PREPERATION

In this work, we used ferroelectric nano – powder of Barium titanate ($BaTiO_3$) of size less than 100nm. This material is used extensively in electronics and microelectronics owing to its excellent ferroelectric, piezoelectric and dielectric properties. The $BaTiO_3$ particles are slightly anisotropic and their size is less than100nm. We have chosen heptane as carrier liquid and oleic acid as a dispersing agent (both from Sigma Aldrich.) $BaTiO_3$ were mixed with oleic acid and heptane in appropriate proportion by weight and then mixed with Palmitate by ultrasonication method [5]. The molecules of dispersing agent attach their polar group to the $BaTiO_3$ surface, while the motion of their non – polar tails builds up the repulsive force between the particles. The ultrasonicator ensures homogeneous distribution of nano – powder in CLC. The mixtures were kept in vacuum for 8 hours for evaporation of heptane completely. The resulting sample contains the small concentration (~1%) of $BaTiO_3$ nano – particles.

3. EXPERIMENTAL TECHNIQUES

The characterization were done by Polarizing Microscopy Studies (PMS), Data Thermal Analysis (DTA), Fourier Transform Infrared (FTIR) Spectroscopy, Ultraviolet Visible (UV) Spectroscopy and Abbe's Refractometer.

3.1 Polarizing Microscopy Studies (PMS)

Polarizing microscope is the most widely used method in identifying different phases Depending on the boundary condition and the type of phase, varies textures which are characteristics of a phase are observed. Usually the textures change while going from one phase to the other LC phases possess characteristic textures when viewed in polarized light under a microscope. These textures, which can often be used to identify phases, result from defects in the textures. When LC, goes from a solid to liquid crystal phase, the degree of length order decreases, which is expressed by a decrease in order parameters. In case of orientational disorder it is possible to see changes between different LC phases of heating and cooling from the textures.

3.2 Data Thermal Analysis (DTA)

Data Thermal Analysis (DTA) is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of sample and reference are measured as a function of temperature. Both sample and reference are maintained at nearly the same temperature throughout. When they undergoes physical transformation such as phase transition heat will need to flow to it than to the reference to maintain both at the same temperature. The amount of heat flow to the sample depends on whether the process is exothermic or endothermic.

3.2 Fourier Transform Infra-red Spectroscopy (FTIR)

FTIR is powerful tool for identifying types of chemical bonds in a molecule by producing an IR absorption spectrum. FTIR is most useful for identifying chemicals that are either organic or inorganic. It is used to identify chemicals from spills paints, polymers, drugs, coating and contaminates. It can be applied to the analysis of types of chemical bonds i.e. functional groups. It is a chemical analytical technique that measures the infrared intensity vs wavelength of light the IR is divided into three regions i.e. far infrared (4 – 400 cm^{-1}) , mid infrared (400 – 4000 cm^{-1}) and near infrared (4000 – 14000 cm^{-1}) IR spectroscopy works because chemical bonds have specific frequencies at which they vibrate corresponding to energy levels. The FTIR spectroscopy detects the vibration characteristics of chemical functional groups in sample, when infrared light interacts with matter, chemical bonds will stretch, contract and bend, so chemical functional group absorbs IR radiation in a specific wave – number range.

3.3 Ultraviolet –Visible (UV) Spectroscopy

UV spectroscopy is an accurate and powerful procedure to analyze a substance. It measures the absorption, transmission and emission of ultraviolet and visible light by matter. Absorption of ultraviolet or visible light causes electron to move from lower to higher energy levels. Because the spectrum of an atom or molecule depends on its electron density level, it is useful for identifying unknown substances.

3.4 Refractive Index (R.I)

In optics, the refractive index of a substance is a number that describes how light, or any other radiation, propagates through that medium. Refractive index of materials varies with the wavelength. In opaque media, the refractive index is a complex number, while the real part describes refraction, the imaginary part accounts for absorption. The concept of refractive index is widely used within the full electromagnetic spectrum, from x –rays to radio waves. It can also be used with wave phenomena other than light. In this case the speed of sound is used instead of that of light and a reference medium other than vacuum.

4. RESULT AND DISCUSSION

Phase transition temperatures and phase sequence of the compound has been presented by PMS and confirmed by DTA.

4.1 Polarizing Microscopy Studies (PMS)

The textures of pure CLC and ferroelectric nano – powder doped CLC obtained by PMS are shown in Figure (1) and Figure (2).

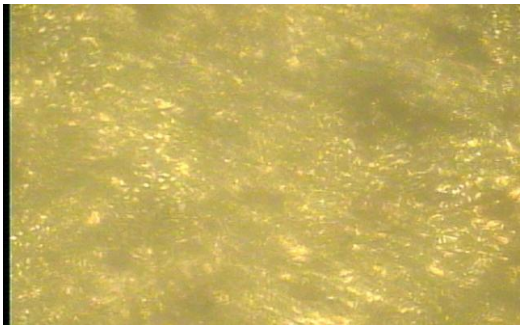

Fig 1(a) Schlieren texture at 40.2 ^{0}C

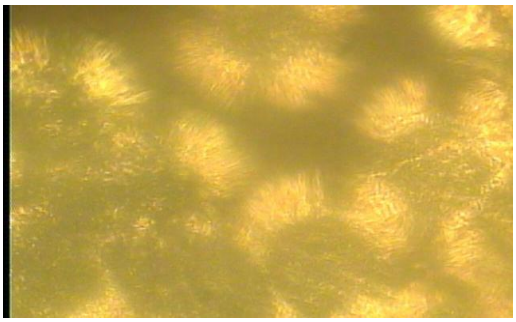

Fig 1(b) Nematic thread like at 58.2 ^{0}C

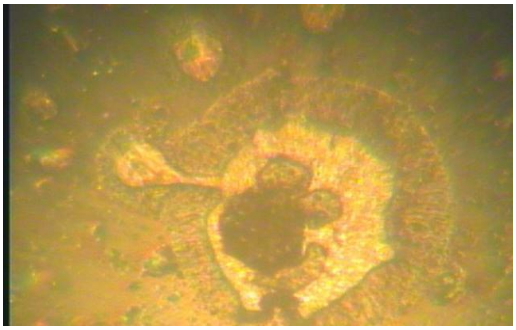

Fig 1(c) Nematic Schlieren at 62.4^{0}C

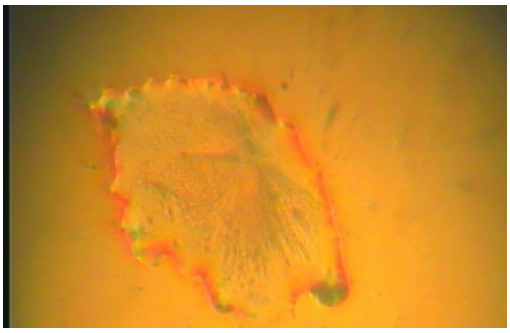

Fig 1(d) Fan like structure at 75.2^{0}C

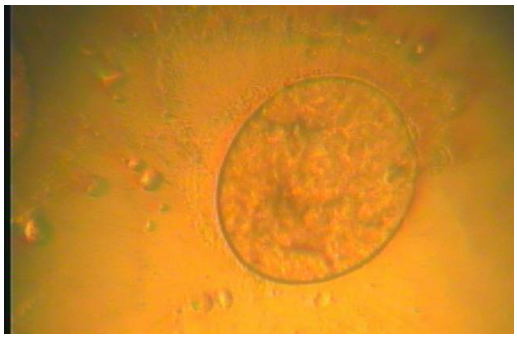

Fig 2(a) Appearance of

Schlieren texture at 77.3^{0}C

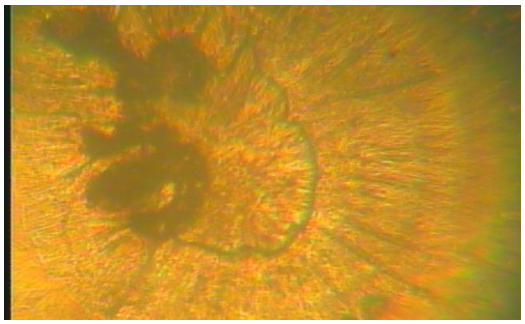

Fig 2(b) Broken fan shaped at 79.5^{0}C

The pure CLC exhibits Nematic phase whereas doped CLC exhibit Smectic A phase. For pure CLC Nematic Schlieren texture appeared at 62.4^{0}C, whereas Broken fan shaped texture for doped CLC Broken fan shaped appeared at 79.5^{0}C

4.2 Data Thermal Analysis (DTA)

The DTA of the pure CLC and doped CLCs in heating and cooling mode are shown in Figure (3) and Figure (4). The transition is given by enthalpy $\Delta S = \Delta H/T$; where ΔH is Transition enthalpy (in J/mole) and T is temperature (^{0}C).

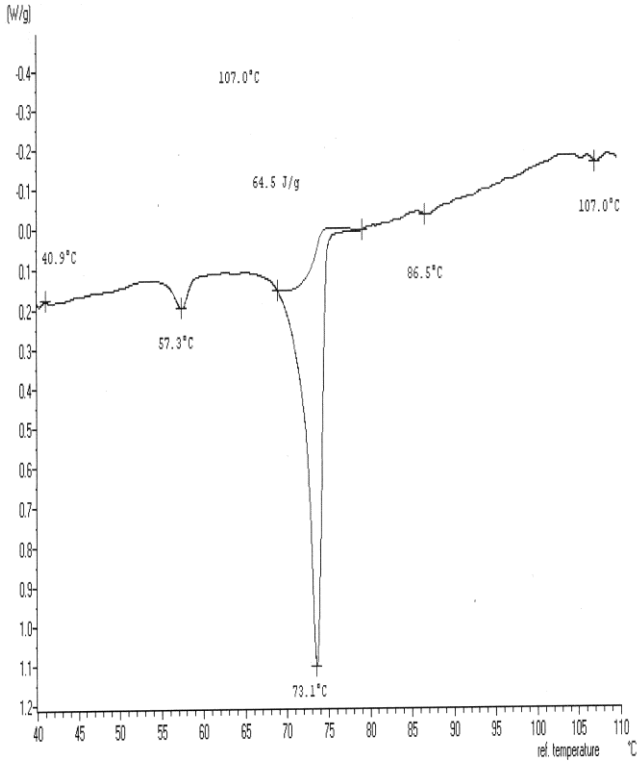

Fig 3(a) DTA of pure CLC in Heating

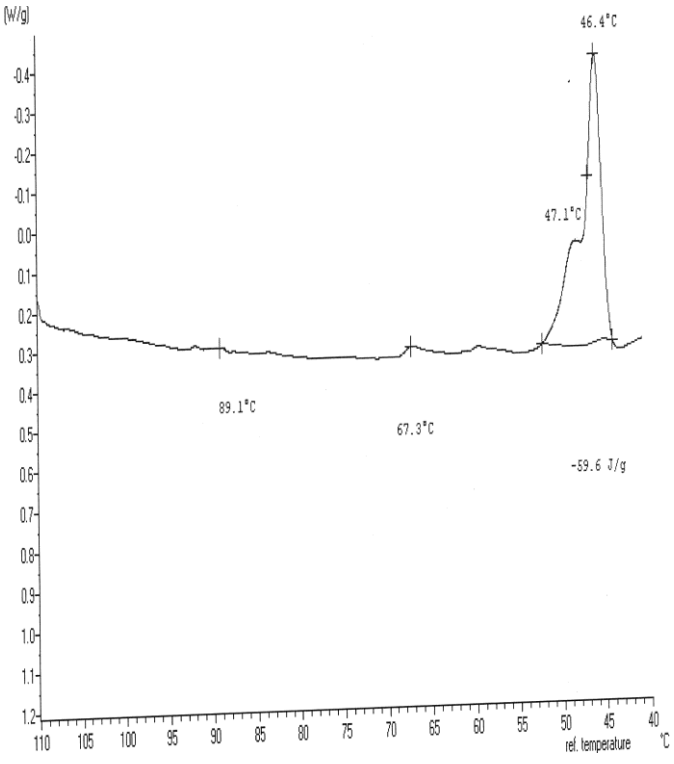

Fig 3(b) DTA of pure CLC in Cooling

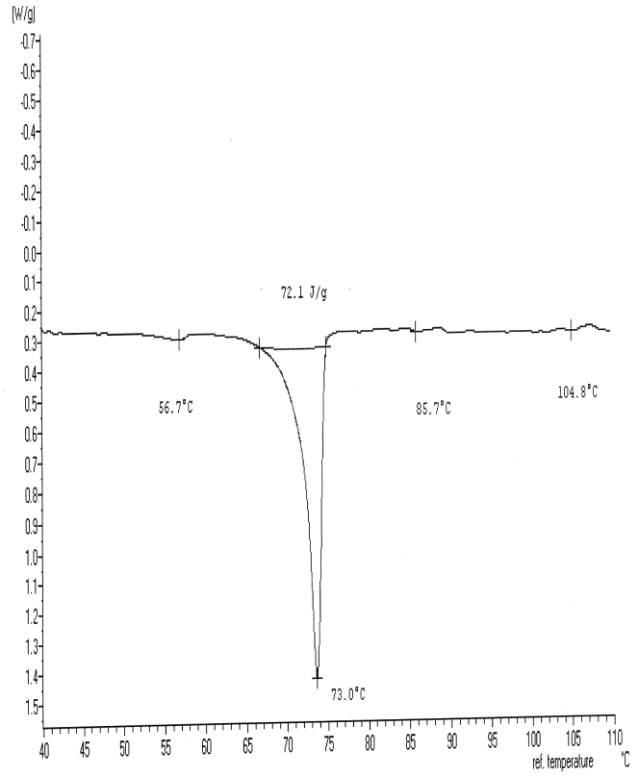

Fig 4(a) DTA of Doped CLC in Heating

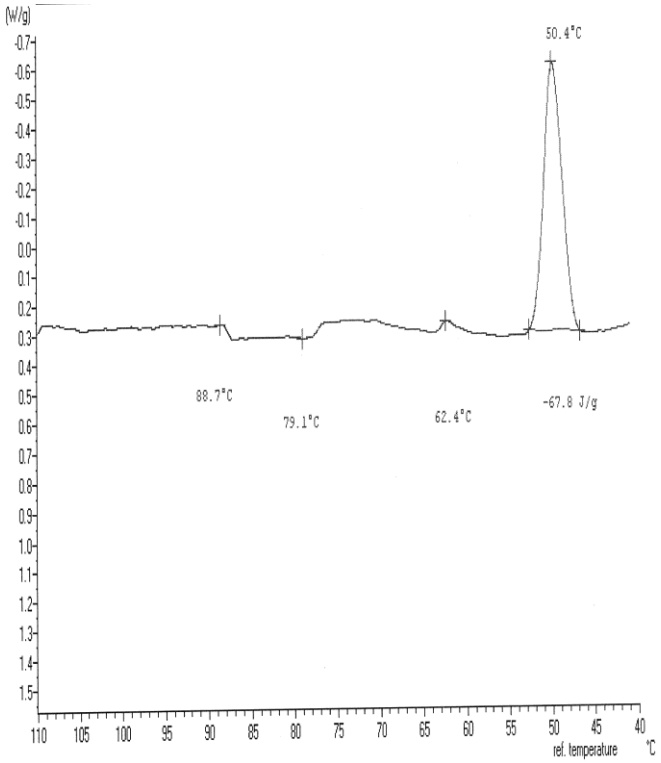

Fig 4(b) DTA of Doped CLC in Cooling

For pure CLC, in heating mode, peak was observed at 73.1^{0}C, whose ΔH value is 64.5 J/g, whereas in cooling mode peak was observed at 46.4^{0}C, whose ΔH value is – 59.6 J/g. For doped CLC, in heating mode, peak was observed at 73.0^{0}C, whose ΔH value is 72.1 J/g whereas in cooling mode peak was observed at 50.4^{0}C, whose ΔH value is – 67.8 J/g. In doped CLC, ΔH and ΔS value is increased.

The changes in peak and ΔH value were found for doped CLC for heating and cooling mode.

Sample	**ΔH (J/g)**	**ΔH (J/mol)**	**ΔS (J/mol^{0}C)**
Pure CLC Heating	64.5	0.1031	0.00141
Pure CLC Cooling	– 59.6	–0.09535	–0.002054
Doped CLC Heating	72.1	0.1153	0.001579
Doped CLC Cooling	– 67.8	–0.1084	–0.002150

The increase in enthalpy shows mesomorphic behaviour.

4.3 Fourier Transform Infra-red Spectroscopy (FTIR)

The FTIR of the pure CLC and doped CLCs are shown in Figure 5 and Figure (6).

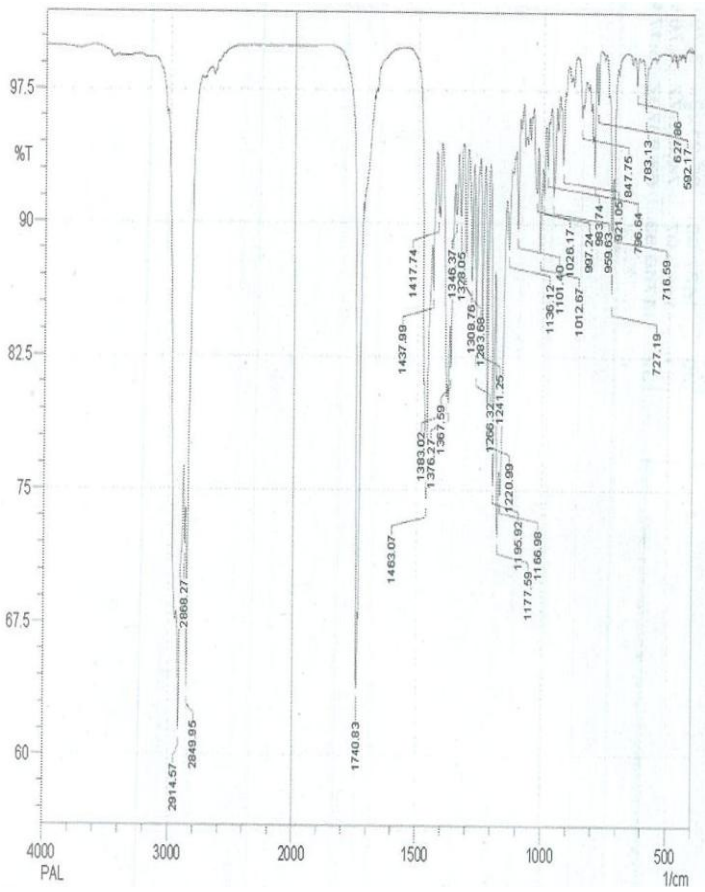

Fig 5(a) FTIR of Pure CLC

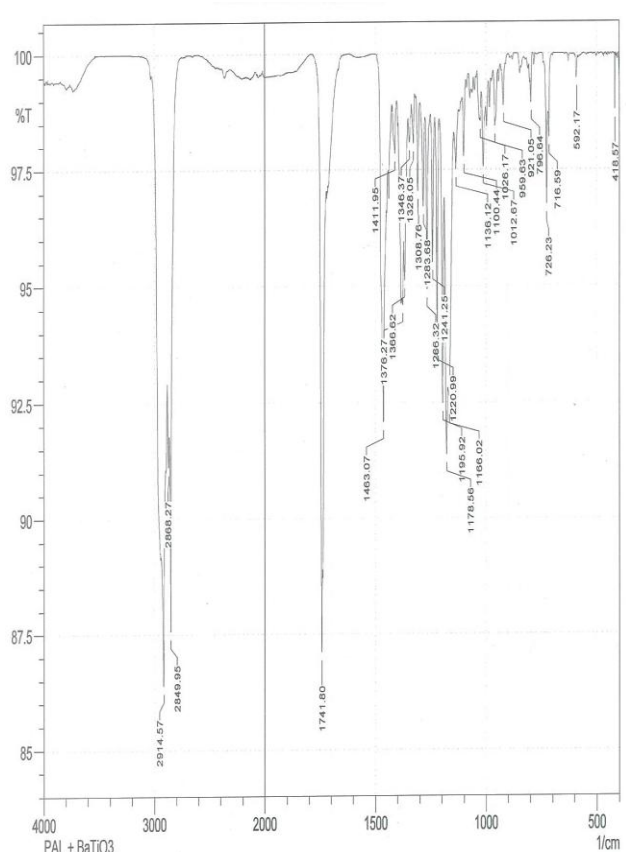

Fig 5(b) FTIR of Doped CLC

The following common wavelengths with different intensities were found.

Sr. No	Wavelength cm^{-1}	Intensity for Pure CLC	Intensity for Doped CLC	Functional group
1.	592.17	96.31132	99.46321	Methyl Ketones
2.	716.59	90.01792	98.19608	1,3 sub Aromatic
3.	796.64	92.68068	98.93572	1,3 Aroma
4.	921.05	93.33347	98.88052	
5.	959.63	91.56318	98.43288	Carboxylic acid dimmer
6.	1012.67	88.45971	97.56456	
7.	1026.17	91.71769	98.54100	Primary Alcohol
8.	1136.12	88.55078	97.49473	Secondary Alcohol
10.	1195.92	75.28096	92.47079	Terrtiary Alcohol
11.	1220.99	78.49799	93.77539	
12.	1241.25	83.45874	95.50976	Aromatic
13.	1266.32	81.87093	94.92632	Carbonate
14.	1283.68	86.69218	96.71443	
15.	1328.05	90.33295	98.06794	Carboxylic acid
16.	1346.37	90.50149	98.09170	
17.	1376.27	79.84473	94.59011	Sulfone
18.	1463.07	74.47177	92.07306	Methyl
19.	2868.27	71.84923	91.12225	Aldehyde

The intensity of doping CLC was found to increase; this is related to the change in dipole that occurs during the vibration. The vibrations that produce a large change in dipole result in a more intense absorption than those that result in a relatively modest change in dipole.

There is also stretching between 1741 to 2948 is observed, which indicates the presence of Aromatic group C=C.

4.4 Ultraviolet –Visible (UV) Spectroscopy

The UV of the pure CLC and doped CLCs are shown in Figure 6 (a) and (b).

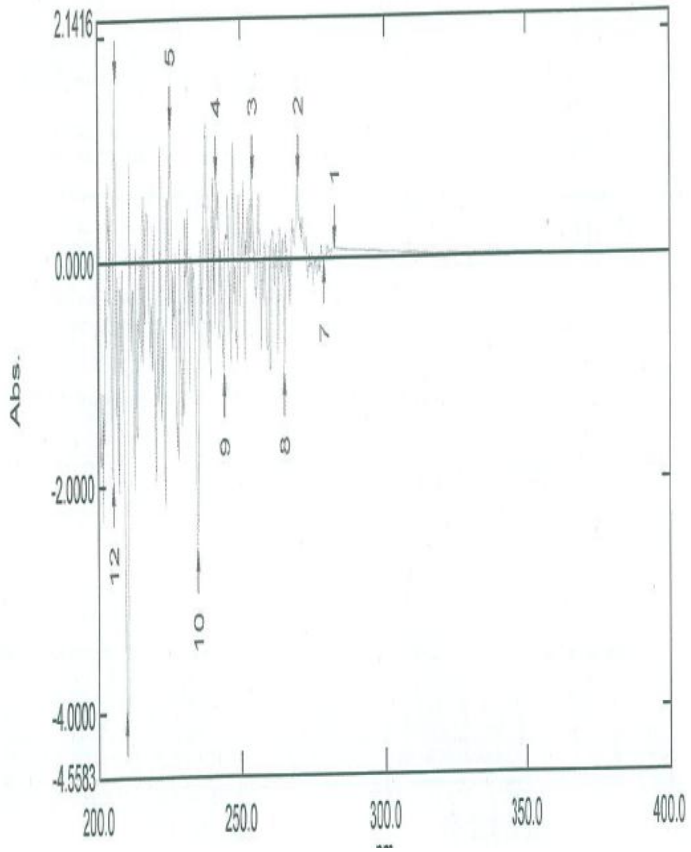

Fig 6(a) UV of Pure CLC

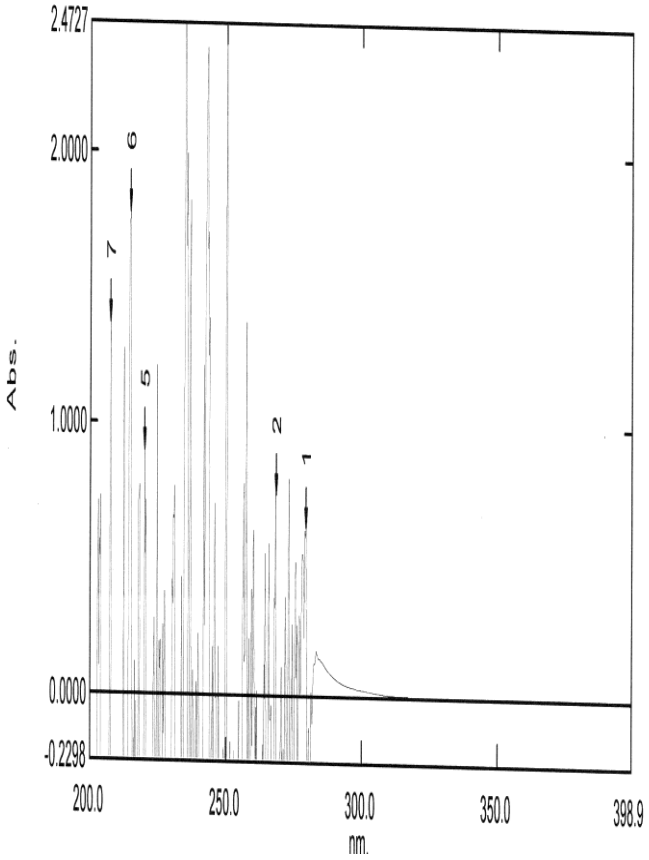

Fig 6(b) UV of Doped CLC

For pure CLC absorbance peak were found in wavelength range from 202 nm to 268.8 nm. The absobobance is maximum at 220.2nm .

For doped CLC absorbance peak were found in wavelength range from 207.4nm to 279.4nm.The absorbance is maximum at 234.8nm.

4.5 Refractive Index

The RI of pure and doped CLC were measured using Abbe's Refractrometer.The RI of pure CLC was found 1.488 whereas the RI for doped CLC were found to be 1.491.This increse in RI after doping CLC with ferroelectric nano – powder of Barium Titanete shows better optical performance of material.

5. CONCLUSIONS

The smectic A phase appears as a typical fan shaped texture or as a homeotropic texture. The mesomorphism of compound is different. It shows nematic phase and smectic phase. At the transition, the smectic A phase forms a schelieren texture which exhibit similarity with fan brushes. The occurance of similarity in the result of an alternating tilt between adjacent layers. The transition temperature were determined by using DTA and measurement the heating rate has small effect on transition and enthalpy.

These changes in the physical properties of doped Cholesteric liquid crystal improves the performance of liquid crystal devices making them operate faster and efficiently. This indicates that low concentration of ferroelectric nano – powder can modify the characteristics of CLCs, which play an important role to design new materials.

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