Performance of TiO_2, ZnO Nano Particles on Optical Properties of Phenyloxy-Cyanobiphenyl Liquid crystal

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ABSTRACT

The Liquid Crystalline Nano composites are prepared by dispersing TiO_2, ZnO nano particles separately in 4-Cyano-4' pentyl oxy biphenyl (5O.CB) liquid crystal in the ratio of 1:100. The characteristic textures exhibited by the composites and their phase transition temperatures are recorded by polarizing optical microscope. The Phase transition temperatures are also carried out by Differential Scanning Calorimeter for confirmation. SEM, EDAX, analysis is done for the characterization. By using Modified Spectrometer, the birefringence of Pure and Liquid Crystalline nano composites is measured in nematic phase. The Orientational Order Parameter of liquid crystalline nano composites are estimated by different methods. The results are discussed.

Keywords: Liquid Crystals, Nanoparticles, Optical textures, phase transition temperature Birefringence, Orientational order parameter.

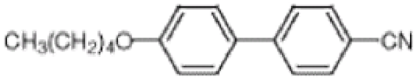
INTRODUCTION

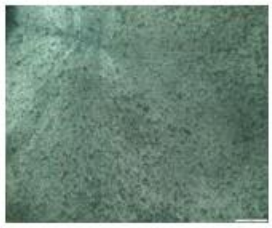
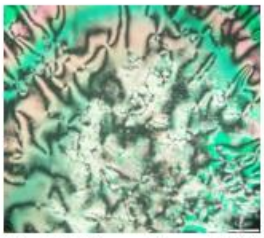
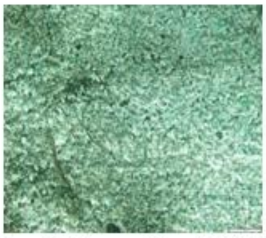
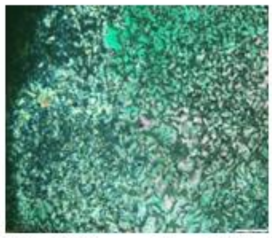
Liquid crystals as fourth state of matter are used for different electro-optic devices. Liquid crystal technology plays a key role at the Note-book, Computer displays, and flat T.V because of showing full range of colour, low Power Consumption using lower space [1]. They are also used at the different areas such as filters [2] Holography [3, 4] digital data storage [5-7] and biosensors [8]. Generally wide temperature of the Liquid crystal phase, high Optical, dielectric anisotropy and fast switching time are required for modern industrial applications. So instead of synthesizing new liquid crystals, by composing liquid crystalline mixtures are using as guest material in host Liquid crystal.

Thus, performance of the device strongly depends on Liquid crystal and guest materials. Nano particles are novel type of guest materials. Doping nano materials in liquid crystals enhances the properties of liquid crystals. In literature different types of metallic nano particles are used to achieve this purpose [9].

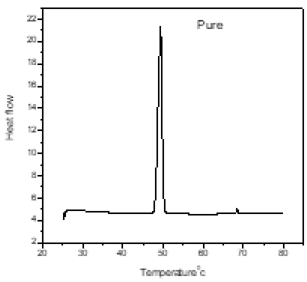
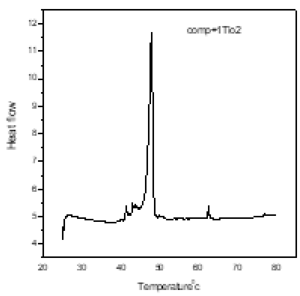
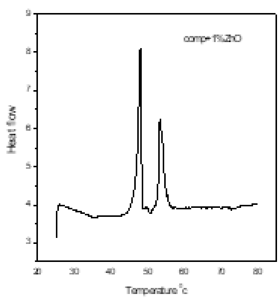
Liquid Crystals acts as tuneable solvents for the dispersion of nano materials and LCs being anisotropic media so they provide good support for the self-assembly of nano materials into large organized structure in multiple dimensions hence liquid crystal mediated self-assembly can be efficiently used to organize different kinds of nano materials into soft and well-defined functional structures. Nanoparticles that are embedded in the host liquid crystals can trap an ion which decreases the ion concentrations, electrical conductivity and improve the electro-optical response of the Liquid crystals. [10]

In the present study the Pentyl-Oxy-cyanobiphenyl is used as the host material and TiO_2, ZnO nano particles separately are used as guest materials, and its characterization is done by SEM, EDAX analysis. By refractive indices and Newton's methods the birefringence of the compounds is measured in nematic phase and the orientational order parameter is estimated. The order parameter is also evaluated by effective geometry parameter and Haller's extrapolation methods. The 5O. CB liquid crystal is procured from TCI.Ltd. Tokyo, Japan. The molecular structure of the compound is shown below.

Name of the sample	Structure of the sample	Molecular formula	Atomic weight
4-Cyano-4' pentyloxybiphenyl		$C_{18}H_{19}NO$	265.36

Textures of pure sample **5O.CB**	Textures of liquid crystal (5O.CB) with dispersed nanoparticals (100:1)	
	TiO_2	**ZnO**
 Fig.1 Crystal at 50.50°*c*	 Fig.3 Crystal at 49.95°*c*	 Fig.5 Crystal at 49.13°*c*
 Fig.2 Nematic at 69.12°*c*	 Fig.4 Nematic at 64.58°*c*	 Fig.6 Nematic at 59.67°*c*

DSC Thermograms

Pure Sample DSC plot	5O.CB Liquid crystal with dispersed nano particles.	
	TiO_2	**ZnO**
		

Transition temperatures of Pure and Nano dispersed compounds

Sl. No.	Compound	Technique	Transition temperatures in c		
			Cr-N.	N-I	Thermal range
01.	5O.CB Pure	DSC	49.25	68.28	19.03
		PCM	50.50	69.12	18.62
02.	5O.CB+ 1% TiO_2	DSC	48.45	63.01	14.56
		PCM	49.95	64.58	14.63
03.	5O.CB+ 1% ZnO	DSC	48.45	56.90	8.45
		PCM	49.13	59.67	10.54

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CHARACTERIZATION OF THE PURE AND NANO PARTICLE DISPERSED SAMPLES

Scanning Electron Microscope

A Scanning electron microscope produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample producing various signals that contain information about topography of the compounds. [11]

A small amount of TiO_2, ZnO nanoparticles dispersed in Liquid crystal compound is taken on a sample holder of the scanning electron microscope. A highly magnified image of the surface of a material is obtained. The SEM gives not only topographical information but also gives the information regarding the composition of the elements in the material [12, 13]. The images of SEM are shown in figure 10. The presence and composition of nano particles in a compound is confirmed from Energy Dispersive X-ray analysis EDAX and shown in fig. The EDAX elucidates the presence of TiO_2, ZnO nano particles, this nano particles in the compound are well established.

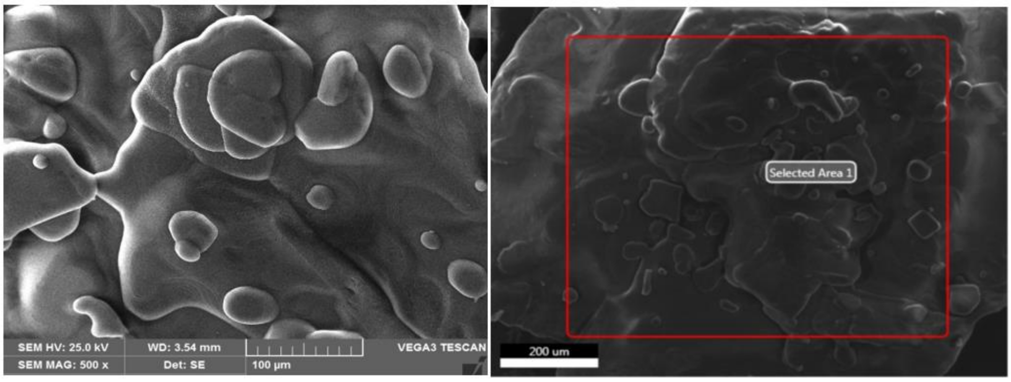

Fig. 10 SEM images of the 5O.CB

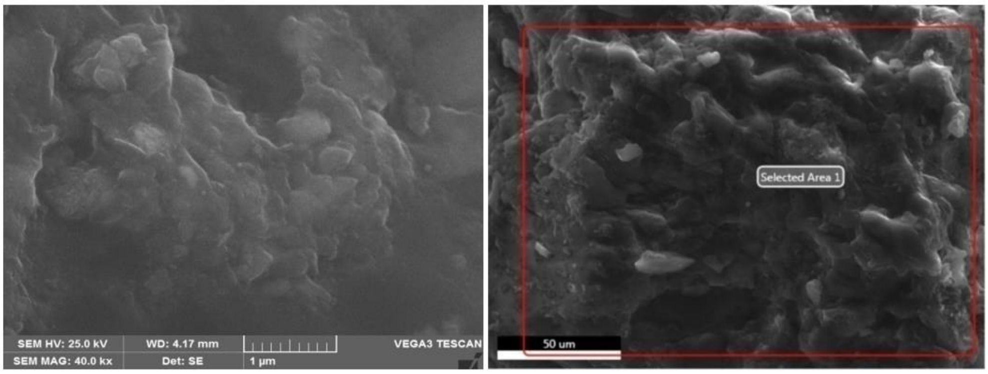

Fig. 11 SEM images of the 5O.CB+1% TiO_2

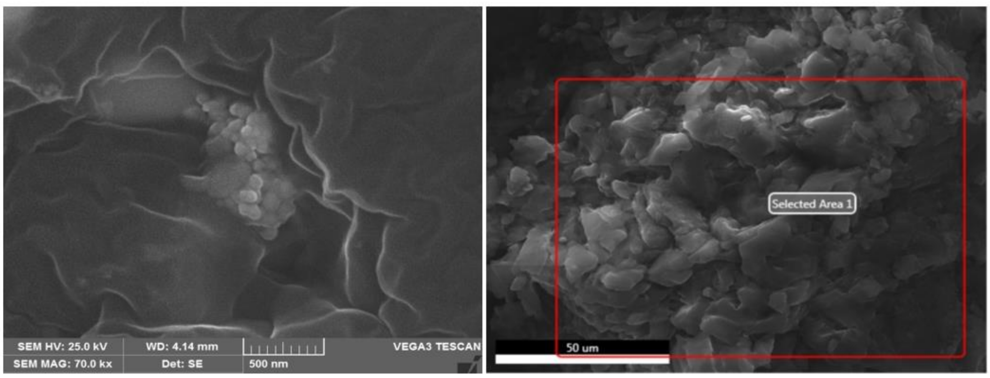

Fig. 12 SEM images of the 5O.CB+1%ZnO

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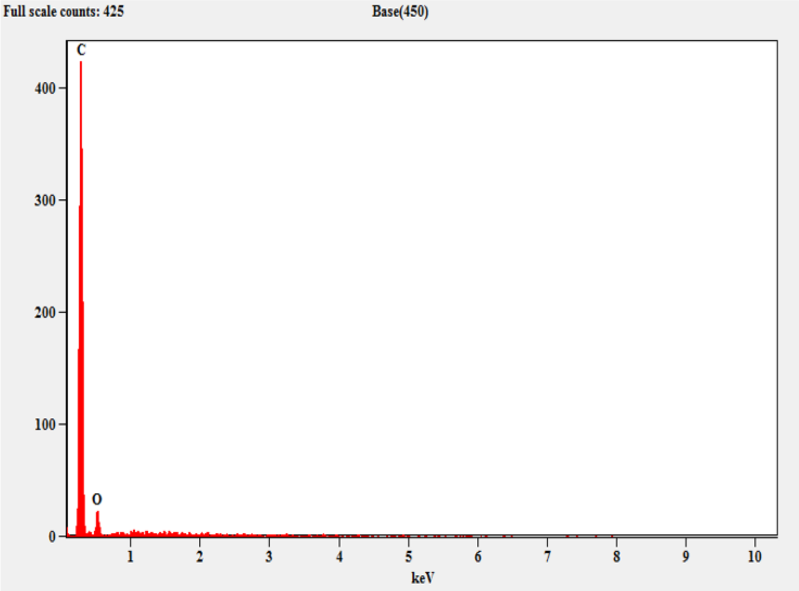
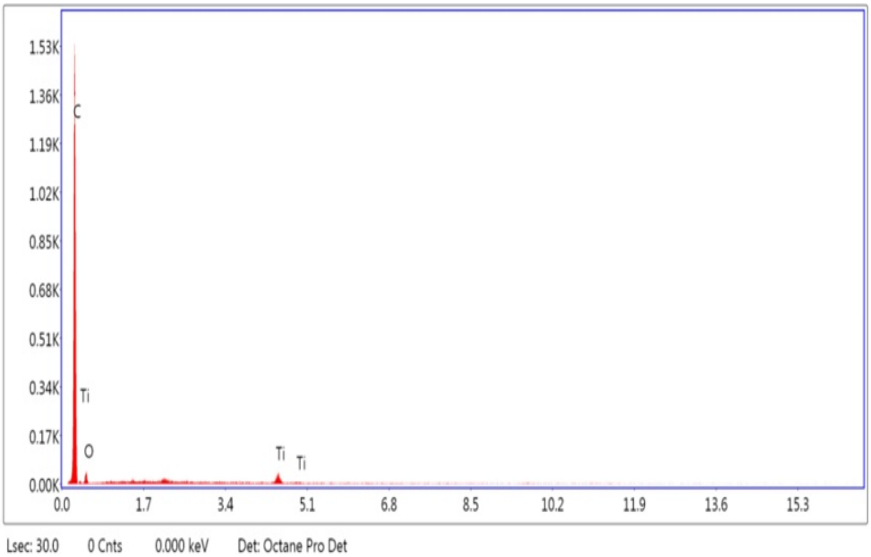


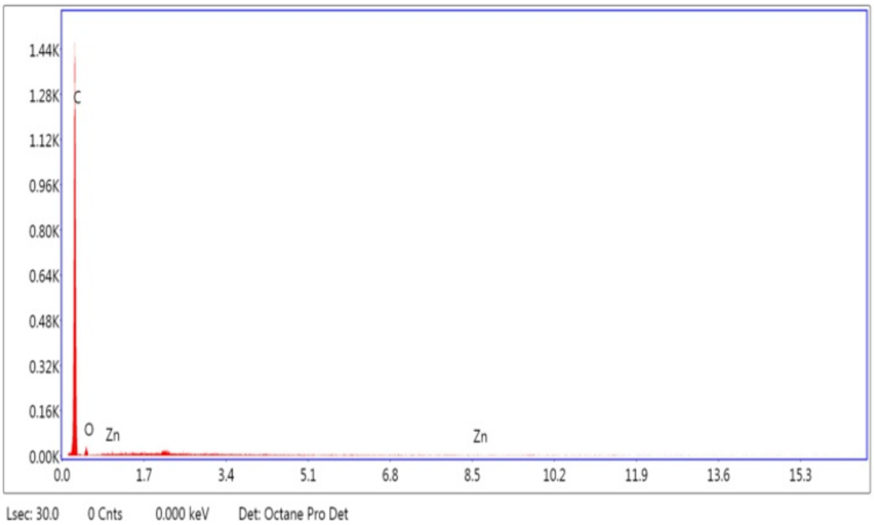
	Weight %	Atom %
C K	99.54	99.65
O K	0.46	0.35
Total	100.00	100.00

Fig. 13 EDAX data of 5O.CB



Element Line	Weight %	Atom %
C K	89.73	92.55
O K	07.80	07.20
TiK	0.98	00.25
Total	100.00	100.0

Fig. 14 EDAX data of 5O.CB+1%TiO_2



Element Line	Weight %	Atom %
C K	92.17	94.02
O K	7.80	0 5.97
ZnK	0.03	00.00
Total	100.00	100.00

Fig. 15 EDAX data of 5O.CB+1%ZnO

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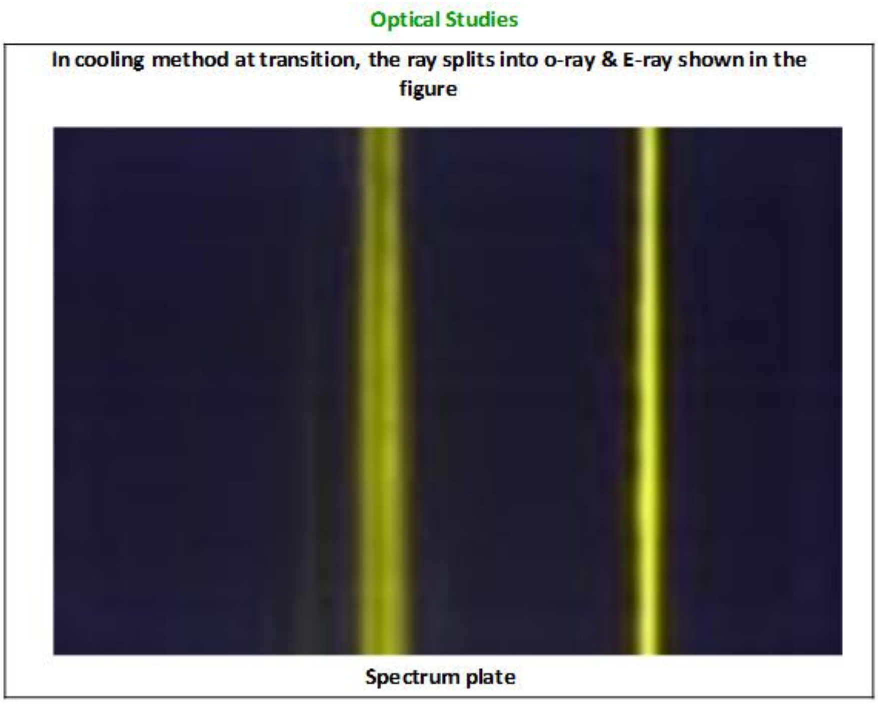
Birefringence studies by refractive indices method

Fig. 16 Modified Spectrometer



The refractive indices of the pure and nano dispersed liquid crystalline compounds are measured at wavelength of 589.3nm using wedge shaped glass cell similar to the one used to obtain birefringence by Haller et. al. [18]. A wedge-shaped glass cell was prepared with two optical flat rectangular glass plates (50mm x 25mm) sandwiched with glass slide of 0.05mm thick which acts as a wedge spacer. The cell is filled with the liquid crystal material. The liquid crystal material in the cell acts as a uniaxial crystal with its optic axis parallel to the edge of the spacer glass plate.

The refractive index practically shows no change in isotropic phase. At the isotropic nematic transformation, the isotropic ray is split into two, one is lower than isotropic value called ordinary ray and another higher than isotropic value called extra-ordinary these are clearly observed in the telescope of modified spectrometer at angle of minimum deviation. In nematic region the n_e increases while n_o decreases with the decrease of temperature. The refractive indices variation with temperature in isotropic and nematic phases for pure and nano dispersed liquid crystalline compounds is illustrated in Figure. 17

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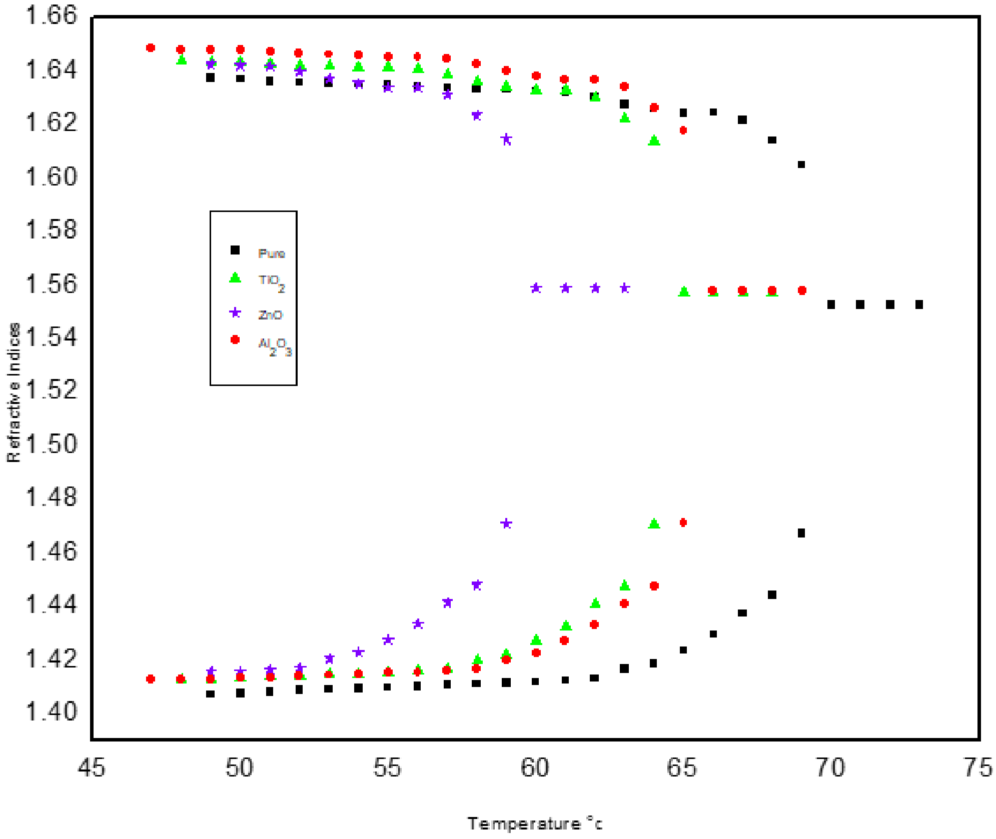

Fig. 17 Temperature variations of refractive indices in 5O.CB+1% eachTiO_2, ZnO

Estimation of Order Parameter S from Birefringence δn

Kuczynski et al [19] proposed a procedure for the determination order parameter S from the birefringence measurements without considering the local field experienced by the molecule in a liquid crystal phase. The birefringence which is a function of temperature is fitted to the following equation.

$$\delta n = \Delta n(1 - \frac{T}{T^*})^{\beta} \quad (1)$$

Where T is the absolute temperature, T^* and β are constants. T is the absolute temperature T^* and β are constants (T^*=T+x) where x varies from 0.001- 4 K and exponent β is close to 0.2. This procedure enables one to extrapolate δn to absolute zero. In practice the three adjustable parameter T^* Δn and β are obtained by fitting the experimental data. For δn the following equation written in the logarithmic form

$$log\delta n = \log(\Delta n) + \beta log\left(T^* - {}^{T}/_{T^*}\right) \quad (2)$$

The Order parameter S is given by

$$S=\frac{\delta n}{\Delta n} \quad (3)$$

Estimation of Order Parameter S from $(1-T/T_c)^{\beta}$

The simple method for the determination of order Parameter is the Haller [21] equation and is given by

$$S= (1-T/T_c)^{\beta} \quad (4)$$

Where T_c is the nematic-isotropic transition temperature and β is the material constant. In evaluating the order parameter using the above equation the β values obtained through regression analysis is used.

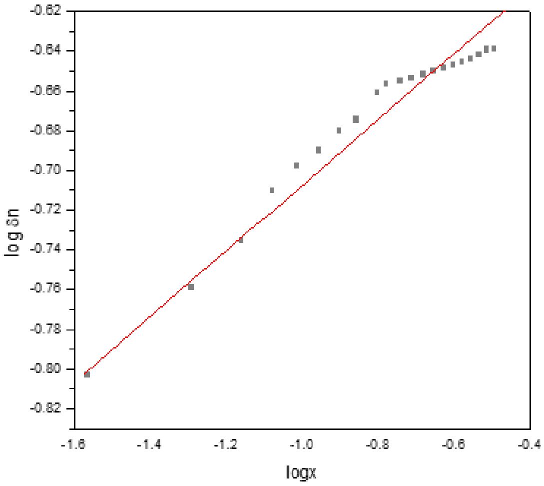

Fig 18 Log-log graphs of 5O.CB RI method

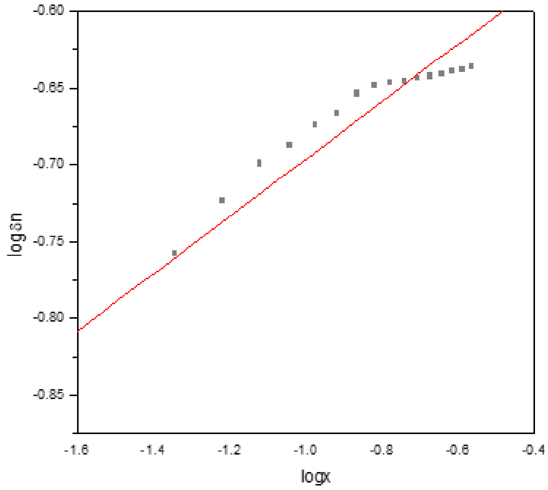

Fig. 19 Log-log graphs of 5O.CB+1%TiO2

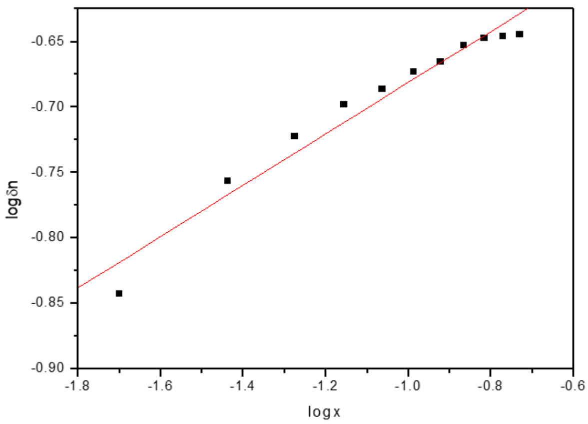

Fig 20. Log-log graphs of 5O.CB+1%ZnO

Estimation of Order Parameter S by Newton's ring method

The experimental setup consists of Plano convex lens of small radius of curvature 1.3mm and plane glass plate which is being placed in hot stage connected to specially designed microcontroller-based temperature and image capturing device. The LC sample whose birefringence is to be measured is placed between the lens and plate. Systems of concentric rings are observed. Newton's rings pattern obtained at temperature is shown in the figure.

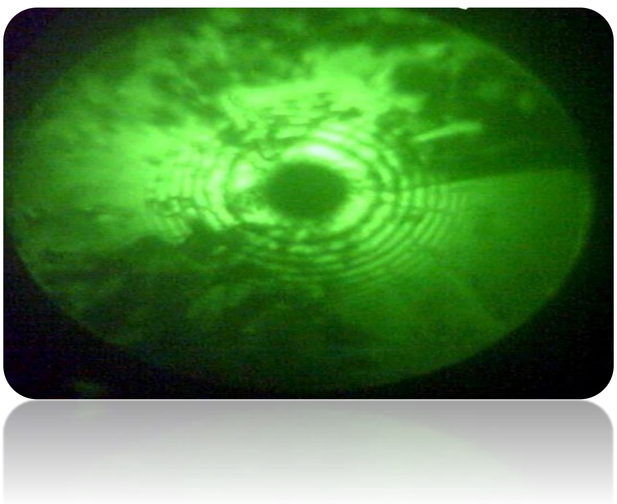

Fig. 21 Newton's rings of the compound 5O.CB at 69° c

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The optical path difference between e-ray and o-ray is given by y, δn which corresponds to ring number k and wavelength λ for a bright fringe is given by

$$\delta n = \frac{k\lambda}{y} \qquad (5)$$

$$Y = \frac{x^2}{2R} \qquad (6)$$

From the equation (5) and (6)

$$\boxed{\delta n = \frac{(2R\lambda)k}{x^2}}$$

Since 2Rλ= C, Cell constant for the given wavelength of light.

$$\boxed{\delta n = \frac{ck}{x^2}} \qquad (7)$$

Where x is the radius of the ring and R, the radius of curvature of the lens used δn can be measured with great accuracy by taking the slope of the straight line drawn between x^2 versus the ring number, k. We can obtain the same result by considering the dark rings also. As the temperature decreases, birefringence δn increases. The method adopted for the estimation of Orientational order parameter from δn given by Kaczynski (21-22)

The Order parameter S is given by

$$S = \frac{\delta n}{\Delta n} \qquad (8)$$

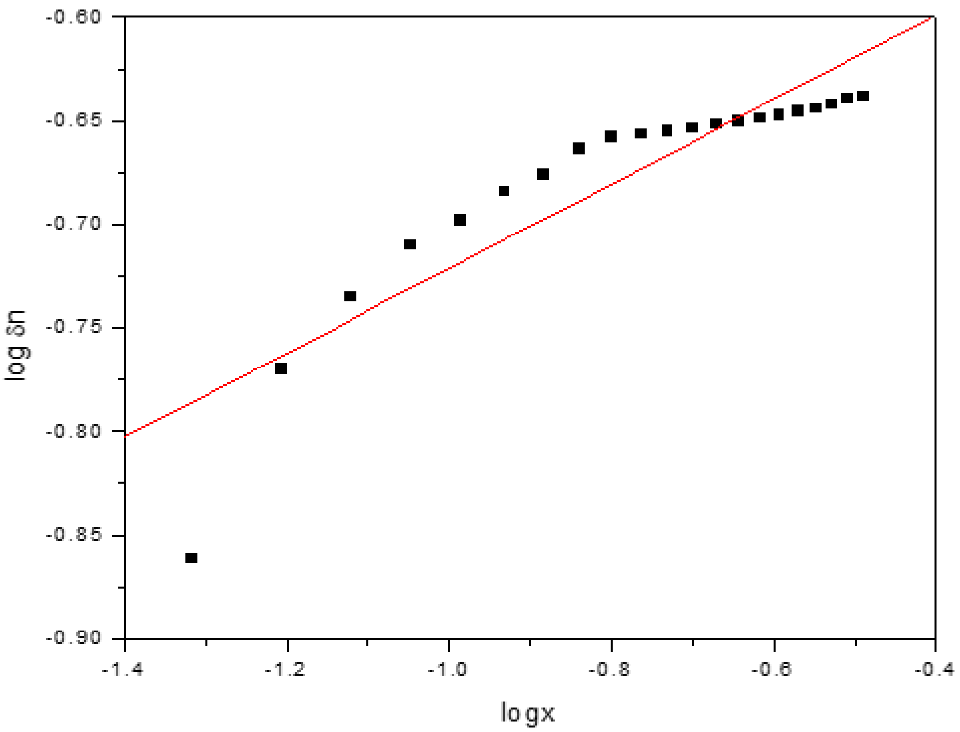

Fig. 22 Log-log graphs of 5O.CB Newton's rings method

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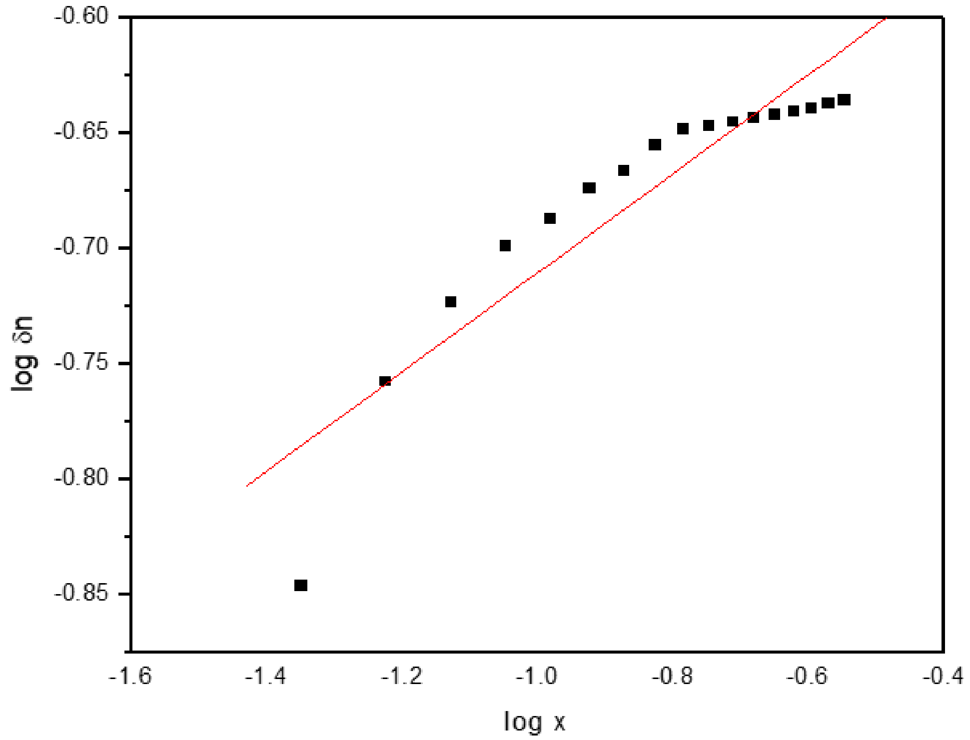

Fig. 23 Log-log graphs of 5O.CB +1%TiO2

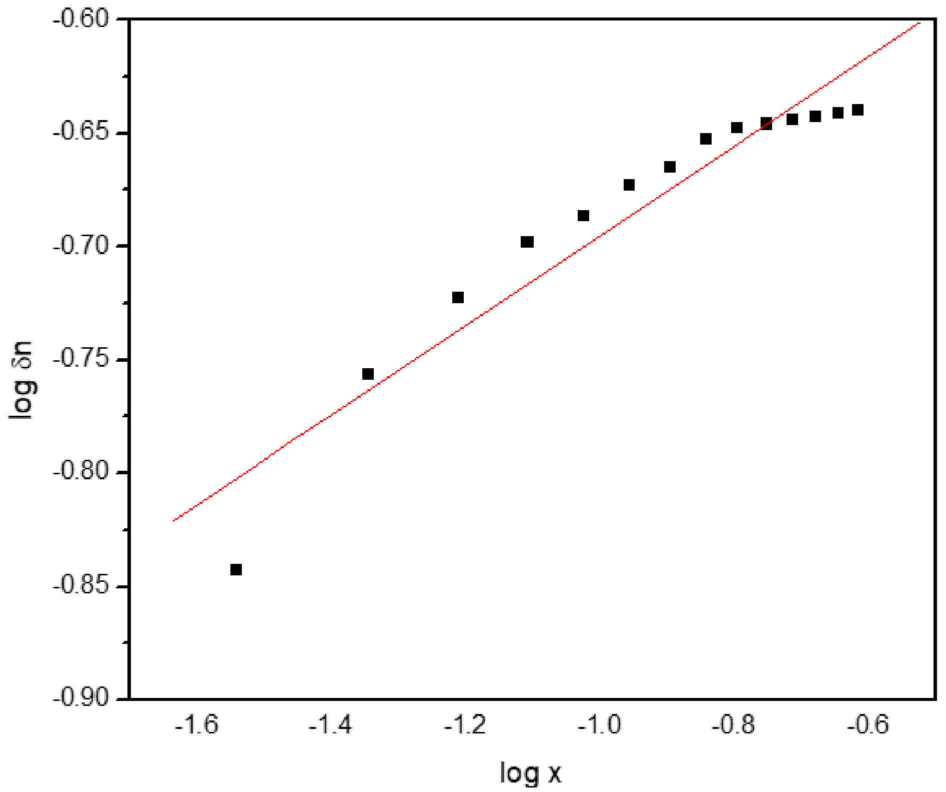

Fig. 24 Log-log graphs of 5O.CB+1%ZnO

Estimation of Order Parameter S from effective geometry parameter α_g

The equation for the determination of the order parameter S involving effective geometry parameter [23] $\alpha_g = n_o/n_e$ is given by

$$S = \frac{3\langle n\rangle(1-\alpha g)}{[2\alpha g+1](\Delta n)} = \qquad (9)$$

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Where $<n^2>$ is the average refractive index obtained from the following equation

$$<n^2>=1/3(n_e^2+2n_o^2)$$

Which slightly decreases linearly the decrease is very small with increase of temperature as follows

$$<n>= C-DT \qquad (10)$$

The variation of order parameter with reduced temperature using (9) is exactly similar to that obtained by using the equation (3). The simplification of equation (9) gives equation 4. Hence, no different plot is drawn using (9) for S. The values C and D are obtained by plotting the temperature and average refractive indices from above equation by linear regression.

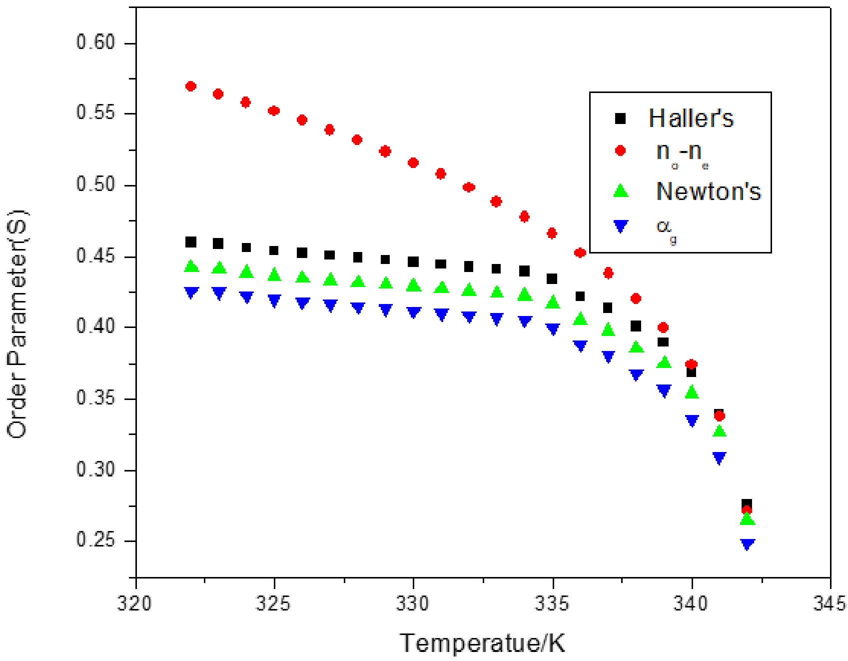

Fig. 26 Order parameter S vs. temperature of Compound 5O.CB

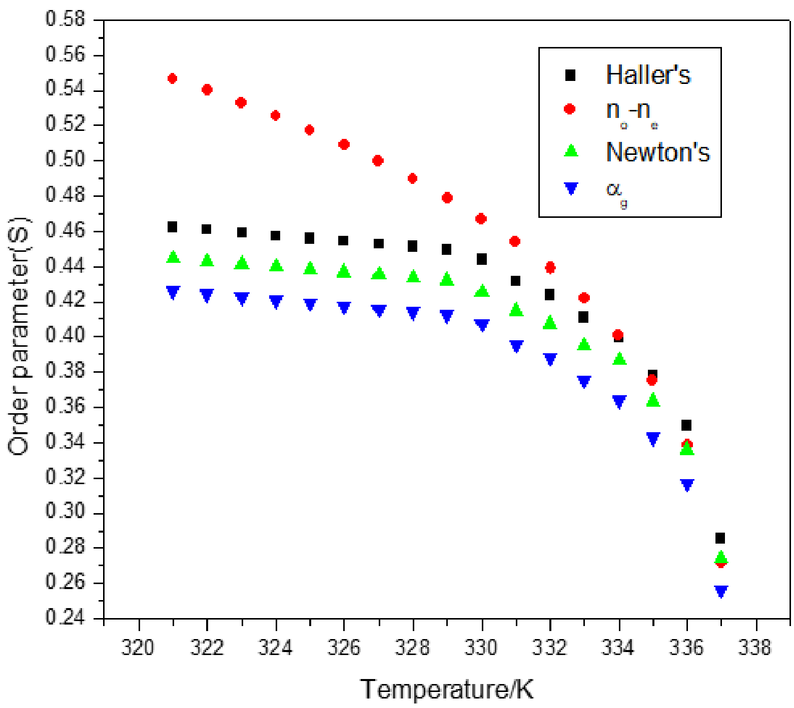

Fig. 27 Order parameter S vs. temperature of Compound 5O.CB+1%TiO_2

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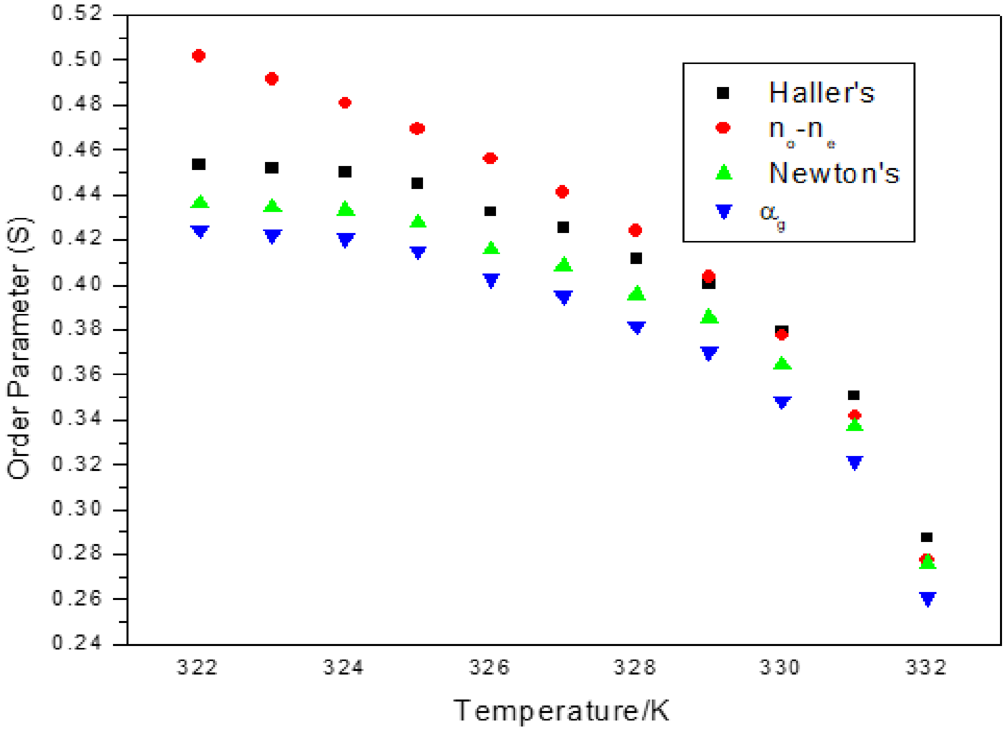

Fig. 28 Order parameter S vs. temperature of Compound 5O.CB+1%ZnO

RESULTS & DISCUSSION

- The Liquid crystal molecules exhibit different phases because the molecular order changes with respect to temperature. The identification and characterization of these phases will provide important information on the pattern and textures of liquid crystals.
- The transition temperature and Optical textures captured by optical polarizing microscope is represented in the fig.1 to 6. The thermal ranges of nematic phases are changed due to the dispersion of nano particles and textures of nematic phases are also changed.
- The transition temperature of the compounds is measured by Differential Scanning Calorimeter (DSC) for confirmation and the DSC thermograms are illustrated in fig.2.1
- SEM and EDAX studies carried out to confirm the composition of the elements in the Liquid crystalline materials and presence of nano particles in the compound is well established.
- The refractive indices of pure and nano dispersed liquid crystalline compounds are measure and its birefringence is estimated.
  a. The birefringence obtained in 5O.CB compound is 0.13763 to 2298.
  b. The birefringence obtained in 5O.CB +1% TiO_2 compound is 14263 to 0.23109.
  c. The birefringence obtained in 5O.CB +1% ZnO compound is 14363 to 0.22919.
- By linear regression analysis method, the birefringence in perfect order is estimated and hence the order parameter is evaluated in nematic phase which is found vary from 27526 to 0.46218.
- The birefringence of the compounds is also measured by Newton's rings method. The Order parameter is varied from 264673 to 0.441923.
- The Order parameter is evaluated by Haller's method using the equation $(1\text{-}T/T^*)^{\beta.}$ The Order parameter obtained is found to be same as that of birefringence and Newton's rings method.
- The effective geometry parameter is very useful in understanding the behaviour of light propagation in liquid crystalline compounds. The effective geometry parameter is a measure of degree of deflection using α_g The order parameter is estimated and compared with the other conventional methods. The order parameter obtained by all the four methods is shown in fig. 26,27and 28. The Order parameter found to be same in all the four methods but there is small deviation from one method to another is due to every method has its own advantage and disadvantage.

CONCLUSIONS

Newton's rings methods are found to be more precise method because in this method the birefringence can also be measured in Semitic phases. From our investigation it is clear that by doping TiO_2, ZnO a nano particle there is increase in order parameter by 7.9% in TiO_2, 8.7% in ZnO

Thus, due to dispersion of nano-particles in Liquid crystal the display properties enhance.

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