

BIREFRINGENCE AND ORDER PARAMETER STUDIES OF ZnO DISPERSED 7oba LIQUID CRYSTALS

***P. Jayaparda**

Department of Physics, Maris Stella College, Vijayawada -520008, India

**Author for Correspondence: jayapradap16@gmail.com*

ABSTRACT

The main concept of the paper was focussed on optical studies of 7oba LC compounds with various weight concentrations (1-2.5wt%) of ZnO dispersed nanoparticles. The synthesized LCs with dispersed ZnO nanoparticles were prepared and further the birefringence measurements were carried out at various wavelengths (460, 500, 570 and 635nm) using wedge shaped cell with modified spectrometer. The birefringence increases with increasing weight concentration of ZnO nanoparticles. Further the order parameter obtained from Kuczynski internal field model, Vuks model, Haller extrapolation model and effective geometry parameter methods were in good agreement. It is found that the order parameter increases with increasing concentration of ZnO nanoparticles. This is due to strong van der Waal's interaction between LC molecules and ZnO nanoparticles.

Keywords: Liquid crystal, ZnO nanoparticles, Birefringence, Order parameter, Modified spectrometer

INTRODUCTION

The special class of materials related to soft matter physics in which the molecules are existed in both properties like order and mobility and show long range orientational orders are named as liquid crystals (LCs) (Collings *et al.*, 1997). The materials exhibit high optical and light scattering properties which depend on the size of the molecules of LCs with different phases such as nematic and smectic (Dmitriev *et al.*, 2010). Based on the properties of LCs like magnetic, electrical, and optical, nowadays liquid crystals are mainly useful in display technology and also in different electro-optical devices (Chandrasekhar, 1992). The combined effect of liquid crystals and nanoparticles (nps) gives a significant attention and a new impact on the LC research (Bisoyi *et al.*, 2011). The inclusion of metal nps into LCs shows the great influence on the physical properties of host medium and promotes new applications in advanced technology (Sikharulidze, 2005). Dispersion of nps into nematic LCs can affect the shape, size and textures and also the phase transition temperatures (Lagerwall *et al.*, 2012). At room temperature, ZnO nps have special features like large bandgap energy, and high exaction binding energy. It is one of the most promising semiconductor materials for the creation of optoelectronic gadgets (Henrich *et al.*, 1994). Dispersion of the zinc- and cadmium-based quantum dots in nematic liquid crystals influence a great change in some optical parameters like birefringence, response time and rotational viscosity are enhanced for the concentration from 0.25 to 1 wt%. The electro-optical properties are also enriched due to doping of ZnO nps in various liquid crystals (Sharma *et al.*, 2019). The authors (Manepalli *et al.*, 2018, Pisipati *et al.*, 2014) suggest that the dispersion of nanoparticles in LCs decrease the transition temperature and improves the contrast ratio and enhances the wide viewing angle in display devices. Different authors (Rao *et al.*, 2009, 2010, 2012, 2013, 2014, 2015, 2017, 2019, P.V. Prasad *et al.*, 2015, Lakshmi *et al.*, 2017, Tejaswi *et al.*, 2020, Madhav *et al.*, 2020, Ravindranadh *et al.*, 2021) distributed their outcomes on various materials in the earlier studies. The author dispersed the ZnO nps into 7oba LCs in low weight concentrations and improves the various parameters like refractive indices, birefringence and orientational order. The values of order parameters are determined in various methods like Kuczynski, Haller Extrapolation, Vuks Isotropic and effective geometry.

MATERIALS AND METHODS

The ingredient like p-(n-heptyloxy) benzoic acid was taken from Sigma Aldrich Lab, USA and used as such without further purification. High-pressure autoclave technique was used to synthesize zinc oxide nanoparticles. 100 mg of 7oba LC material was taken in 5 ml beaker, and dissolved in ethyl alcohol. Later, the solution was stirred for about 1 h with the aid of magnetic stirrer (700 revolutions per minute) at 60°C temperature. After stirring, 1 wt% of ZnO nps were introduced into the above solution, and again the mixture was stirred for about 45 minutes by raising the temperature nearly 100°C, then ethyl alcohol was evaporated. Finally, the mesogenic material of LC compound, 7oba with 1wt% ZnO nps was formed in the isotropic state. The same procedure was followed for other concentrations of ZnO nps (1.5 to 2.5 wt%). The values of display parameters such as refractive indices, birefringence (δn) and order parameter (S) were estimated with the aid of modified spectrometer (SDTECHS make 6336).

RESULTS AND DISCUSSION

Calculation of refractive indices using Modified Spectrometer: The RI (refractive index) Values of 7oba, pure with dispersed ZnO nps are determined using a wedge-shaped glass cell with the aid of modified spectrometer (Kim *et al.*, 2011) (SD Techs SDMS 6336). The perfection in the measured RI values is ± 0.0005 and exactness of the temperature of heating block is $\pm 0.1^\circ\text{C}$. The state at which temperature is varied from heating mode to cooling mode, the deviated ray separates into two rays one is e-ray (extraordinary ray having higher value of n_{iso}) and the other is ray known as O-ray (ordinary ray having lower value of n_{iso}) and their corresponding refractive indices (n_e and n_o) are calculated with variation of temperature in nematic region of 7oba pure, dispersed with ZnO nps at various wavelengths in visible region 460, 500, 570 and 635 nm are shown in Fig 1(a-e). The RI values of e-ray and o-ray are increased with increasing concentration of ZnO nps with respect to wavelength with decreasing temperature.

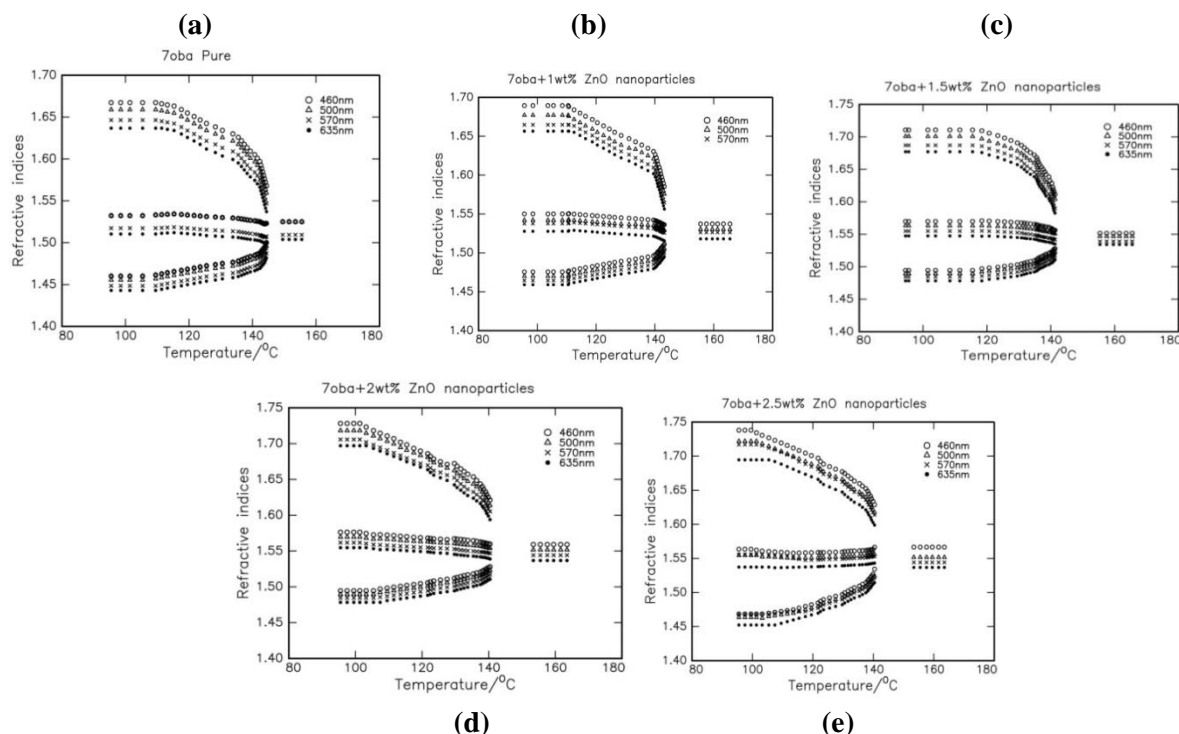


Fig.1: Refractive indices of e-ray and o-ray versus temperature of (a) pure 7oba, and 7oba with dispersed ZnO nps at various concentrations (b)1 wt%, (c) 1.5 wt%, (d) 2 wt%, (e) 2.5 wt%

Measurement of Birefringence (δn): The phenomena exhibit a key role with increasing the display parameter known as birefringence. The difference in the RI values of e-ray and o-ray results birefringence. The RI values of e-ray & o-ray increases with the inclusion of ZnO nps concentration from 1 to 2.5 wt%. As the concentration of induced ZnO nanoparticles increased, the transition temperature of nematic phase is reduced. The value of birefringence increases at which the phase changes from I-N transition. For 7oba ZnO nps (1-2.5 wt%) in comparison with the pure 7oba, δn increases from 0.0066 to 0.0624 (3.085 – 30.11) at 460 nm, 0.0035 to 0.055 (1.729 – 27.04%) at 500 nm, 0.0022 to 0.0506 (1.110 - 25.56%) at 570 nm and 0.0036 to 0.0485 (1.85 – 25.03%) at 635 nm respectively. The pictures with respect to wavelength (460, 500, 570, 635 nm) are presented in Fig. 2(a-i) and related data is presented in Table 1.

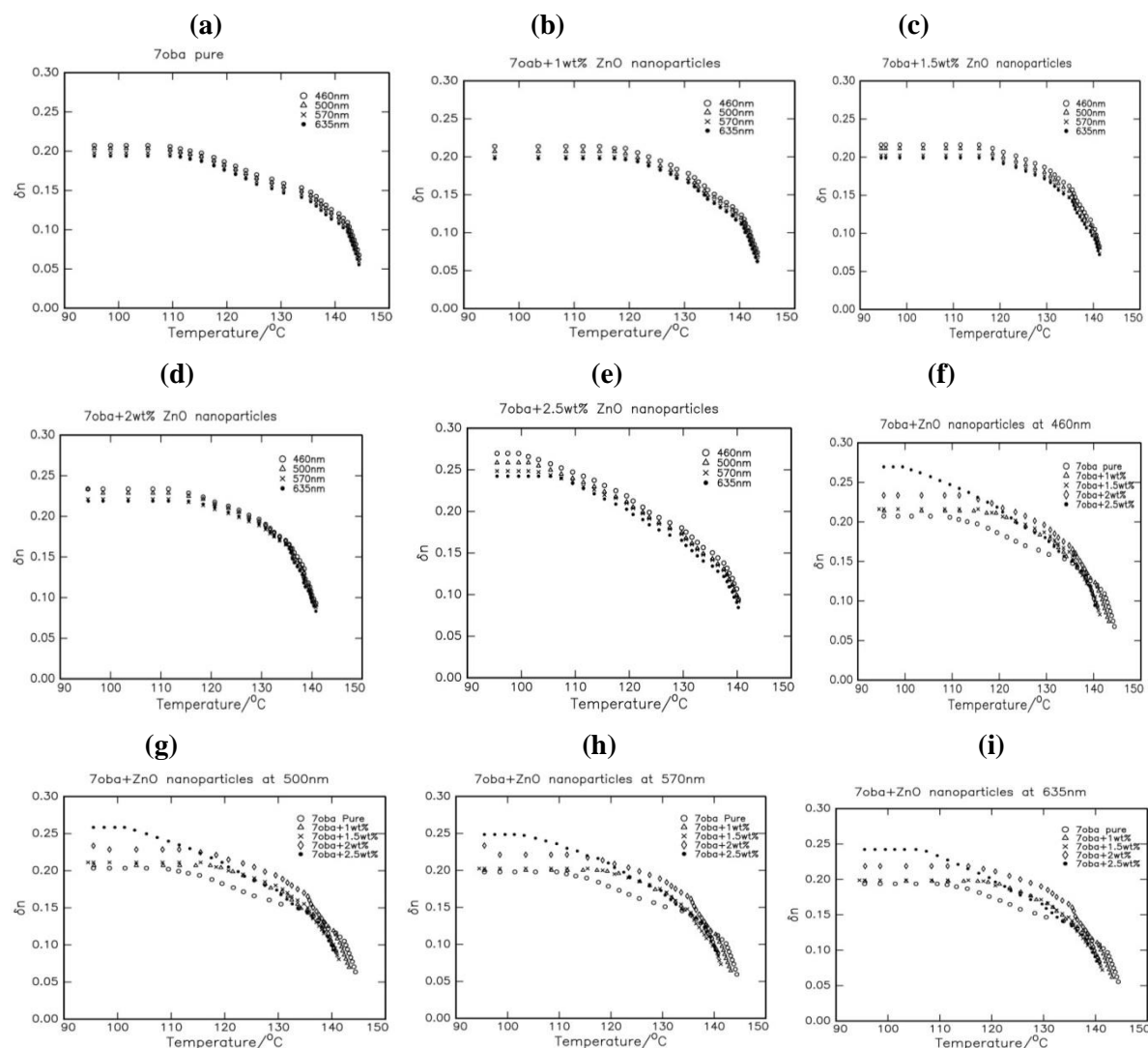


Fig. 2: Temperature versus birefringence (δn) of (a) pure 7oba, and 7oba with dispersed ZnO nps (460, 500, 570, 635 nm) at various concentrations (b) 1 wt%, (c) 1.5 wt%, (d) 2 wt%, (e) 2.5 wt%, (f) 7oba with different weight concentrations at 460 nm, (g) 500 nm, (h) 570 nm, (i) 635 nm

Table 1: Percentage increment of birefringence (δn) of 7oba pure with induced ZnO nps from 1-2.5wt%

Compound+ZnO nps	460 nm	500 nm	570 nm	635 nm
7oba+1 wt%	3.085	1.729	1.110	1.858
7oba+1.5 wt%	4.348	3.835	2.320	2.210
7oba+2 wt%	12.69	12.38	11.72	12.85
7oba+2.5 wt%	30.11	27.04	25.56	25.03

Order parameter studies: After finding the different optical parameters like RI, δn , another study of LC materials known as order parameter and its average direction is always oriented about the optic axis in LC molecules. The values of S are measured from the values of RI data by various procedures namely Kuczynski, Vuks, Haller and also from Effective geometry parameter models which are presented in table 2. An improvement in the alignment of the molecules of LCs can be achieved due to the induced of ZnO nps in 7oba LC.

Kuczynski Model: For the measurement of S values, the birefringence values (δn) are taken in the nematic phase and not taken by the local field experienced by molecule of LCs. The way of finding of S values are so easy and this model was developed by Kuczynski. The birefringence (δn) is determined by simple equation and it is related to temperature $\delta n = \Delta n \cdot \{1 - (T/T^*)\}^\beta$. Here, the constants are T^* and β , T is related to absolute temperature (T^* is about 1-4 K higher than the clearing temperature and the exponent β is close to 0.2). To extrapolate the value of δn at the temperature of absolute zero adjust the three parameters T^* , Δn and β with the experimental data. For fitting these parameters, the value of δn is taken in log form so that it can be written as:

$$\text{Log } \delta n = \text{log } \Delta n + \beta \text{ log } \{1 - (T/T^*)\} \quad \text{-----} \quad (1)$$

The simplest equation of measurement of value of order parameter S is $S = \delta n / \Delta n$, in these terms having the special names like Δn is the birefringence in perfect order, $\delta n = (n_e - n_o)$, here the values are determined only in the nematic phase.

Haller Extrapolation model: As the birefringence value is increased, the order parameter is increased and it is in linear relationship. The values of S are calculated using Haller's model with the simple equation and it is temperature dependent. The equation is mentioned below:

$$S_{\text{Haller}} = \left(1 - \frac{T}{T_{\text{NI}}}\right)^\beta \quad \text{-----} \quad (2)$$

Where T_{NI} , represents the clearing temperature of I-N phase transition and β is the slope. These values are meant for perfectly liquid crystalline state of LC materials of order $S=1$ which thermally influences the behavior of LC materials.

Effective Geometry model: α_{eg} is the ratio of n_o/n_e , from the below equation, the order parameter can be calculated the model is named as Effective geometry.

$$S_{\alpha_{\text{eg}}} = \frac{3\sqrt{\langle n^2 \rangle}}{(\Delta n)_o} \left(\frac{1 - \alpha_{\text{eg}}}{1 + 2\alpha_{\text{eg}}} \right) \quad \text{-----} \quad (3)$$

Vuks isotropic model: From the equation (4), the values of order parameter can be calculated by Vuks' isotropic field model.

$$S_{\text{vuks}} \frac{\Delta \alpha}{\alpha} = \frac{n_e^2 - n_o^2}{\langle n^2 \rangle - 1} \quad \text{-----} \quad (4)$$

To find the value of $\Delta\alpha/\alpha$, a graph is drawn between $\text{Log} \frac{n_e^2 - n_o^2}{\langle n^2 \rangle - 1}$ and $\log (1 - T/T_{NI})$. The graph gives a

linear relationship between the above two terms which is named as scaling factor, by simply extrapolate this graph at absolute temperature $T = 0$ K, the intercept value gives the value of scaling factor. Here, $\Delta\alpha$ and $\Delta\alpha$ ($\alpha_{\parallel} - \alpha_{\perp}$) are the mean value of molecular polarisabilities of LC molecules and α is the anisotropy, the order parameter can be determined at different temperatures.

It is clear that the data of δn of 7oba LC compound are increased in the nematic phase with the induced of ZnO nps in low weights. The order parameters of 7oba LC compound are increased with increasing the concentration of ZnO nps. Further, the order parameter values are also improved from higher wavelength to lower wavelength in the visible region in the four internal field models. From the above observations, since the zinc oxide nps are larger in size and these are having high dipole moments than nematic LC, which produces more torque than nematic LCs. This torque is used to orient the molecules of LCs enhances the birefringence and ordering of LC molecules. The ordering of LC system are calculated in the four internal field models also observed with induced of ZnO nps (1-2.5 wt%). The related figures are shown in Fig. 3(a-d). The values of order parameter versus with temperature for 7oba pure and with dispersion of ZnO nps in various concentrations in different methods at different wavelengths are shown in Fig. 4

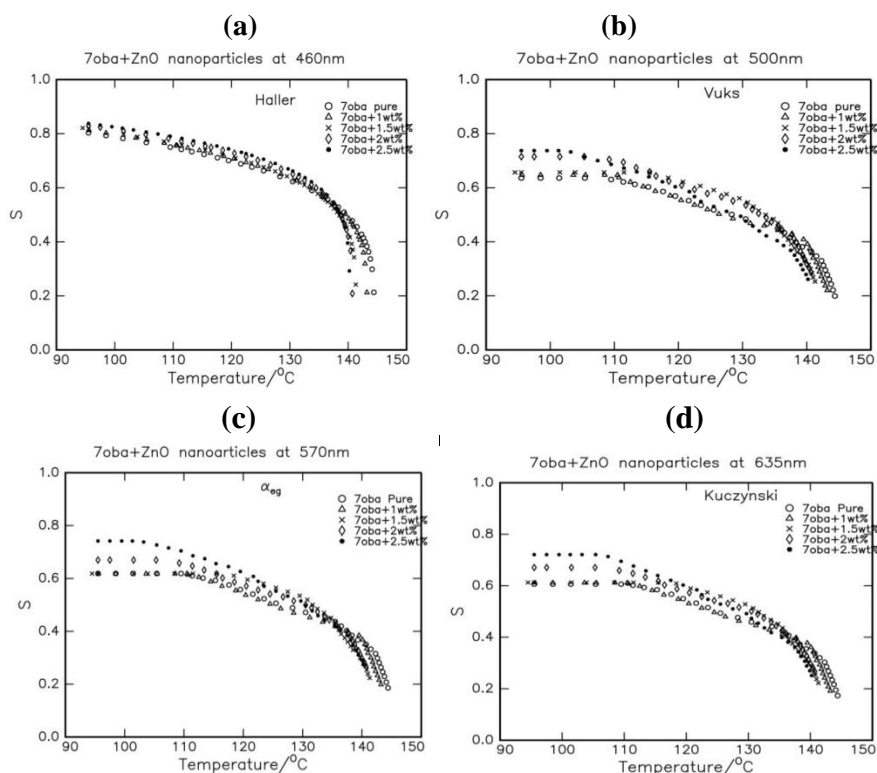


Fig. 3: Temperature versus order parameter (δn) of pure 7oba with dispersed ZnO np (1-2.5 wt%) at various wavelengths (a) 460 nm, (b) 500 nm, (c) 570 nm, (d) 635 nm

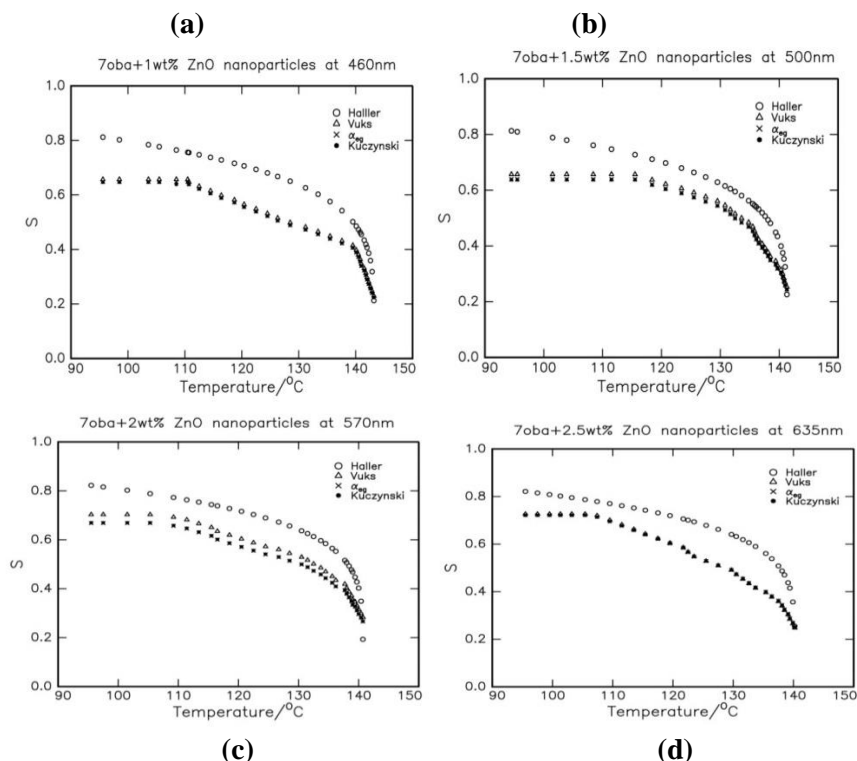


Fig. 4: Temperature versus order parameter (δn) of pure 7oba with dispersed ZnO np (1-2.5 wt%) at various wavelengths (a) 460 nm, (b) 500 nm, (c) 570 nm, (d) 635 nm in all models

Table 2: The values of order parameter, S of molecules of 7oba pure and with dispersion of ZnO nps in different low weight concentrations from 1-2.5 wt% in the stabilized nematic thermal region for various wavelengths in the visible region in different internal field models

Compound+ZnO nps	Wavelength	Values of order parameter, S in			
		Kuczynski	Alpha eff.	Haller	Vuks
7oba pure	460 nm	0.6386	0.6399	0.8031	0.6407
	500 nm	0.6325	0.6337	0.7986	0.6358
	570 nm	0.6176	0.6188	0.7923	0.6287
	635 nm	0.6061	0.6073	0.7862	0.6235
7oba+1 wt%	460 nm	0.6494	0.6483	0.8120	0.6567
	500 nm	0.6354	0.6367	0.8076	0.6468
	570 nm	0.6362	0.6277	0.8003	0.6355
	635 nm	0.6114	0.6131	0.7977	0.6315
7oba 1.5 wt%	460 nm	0.6596	0.6510	0.8210	0.6617
	500 nm	0.6477	0.6391	0.8132	0.6568
	570 nm	0.6436	0.6381	0.8051	0.6420
	635 nm	0.6226	0.6237	0.8039	0.6371
7oba 2 wt%	460 nm	0.6942	0.6959	0.8310	0.7228
	500 nm	0.6843	0.6851	0.8273	0.7150
	570 nm	0.6681	0.6697	0.8225	0.7029
	635 nm	0.6708	0.6647	0.8157	0.7068
7oba 2.5 wt%	460 nm	0.7536	0.7762	0.8378	0.7581
	500 nm	0.7416	0.7665	0.8302	0.7372
	570 nm	0.7374	0.7417	0.8243	0.7229
	635 nm	0.7209	0.7220	0.8215	0.7263

CONCLUSIONS

The optical studies of 7oba LC compounds are studied with various weight concentrations of ZnO dispersed nanoparticles. The values of RI are taken from modified spectrometer of 7oba nanocomposites at various wavelengths in the visible region. Due to the inclusion of ZnO nps in 7oba the LC molecules can achieve improvement in the alignment. The Refractive indices and birefringence are increased with ZnO nps in small amounts and is responsible for the enhancement of order parameter at four wavelengths such as 460 nm, 500 nm, 570 nm and 635 nm in the visible region of nematic phase in all optical methods (Kuczynski. Vuks, effective, Haller). The increment in the above optical parameters is more responsible for the invention of display devices.

REFERENCES

- P.J. Collings, M. Hird (1997).** Introduction to Liquid Crystals Chemistry and Physics, Taylor & Francis, London.
- S.M. Dmitriev, V.P. Dick, N.N. Kostyuk, T.A. Dick, V.A. Loiko (2010).** *Journal of Semiconductor Physics, Quantum Electronics & Optoelectronics*, **13(2)** 132-136.
- S. Chandrasekhar (1992).** Liquid crystals, 2nd ed. Cambridge (UK), Cambridge University Press.
- H.K. Bisoyi, S. Kumar (2011).** Liquid-crystal nanoscience: an emerging avenue of soft self-assembly. *Journal of Chemical Society Reviews*, **40** 306-319.
- D. Sikharulidze (2005).** Nanoparticles: An approach to controlling an electro-optical behavior of nematic liquid crystals. *Journal of Applied Physics Letter*, **86** 033507.
- J.P.F. Lagerwall, G. Scalia (2012).** A new era for liquid crystal research applications of liquid crystals in soft matter nano-,bio-and micro technology. *Journal of Current Applied Physics*, **12** 1387-1412.
- V.E. Henrich, P.A. Cox (1994).** The surface science of metal oxides, Cambridge University Press, Cambridge.
- S. Supreet, K. Kumar, R. Pratibha (2017).** Enhanced stability of the columnar matrix in a discotic liquid crystal by insertion of ZnO nanoparticles. *Journal of Liquid Crystals*, **40(2)** 228-236.
- A. Sharma, P. Malik Ravindra Dhar, Pankaj Kumar (2019).** Improvement in electro-optical and dielectric characteristics of ZnO nanoparticles dispersed in a nematic liquid crystal mixture. *Bulletin of Material Science*, **42** 215-227.
- R.K.N.R. Manepalli, G. Giridhar, P. Pardhasaradhi (2018).** Influence of ZnO nanoparticles dispersion in liquid crystalline compounds-experimental studies. *Journal of Materials today Proceedings*, **15** 2666-2676.
- V.G.K.M. Pisipati, D. Madhavi Latha, P. Pardhasaradhi, P.V. Datta Prasad (2014).** Dispersive power and crossover temperature, TCO, of two polar nematic liquid crystals in the visible spectral region. *Journal of Liquid Crystal Today*, **23(4)** 70-76.
- M.C. Rao, O.M. Hussain (2009).** Growth and characterization of tetravalent doped LiCoO₂ thin film cathodes. *Indian Journal of Engineering and Materials Sciences*, **16** 335-340.
- M.C. Rao, O.M. Hussain (2009).** Optical and electrical properties of laser ablated amorphous LiCoO₂ thin film cathodes. IOP Conference Series: *Materials Science and Engineering*, **2** 012037.
- M.C. Rao (2010).** Microstructural and electrochemical properties of LiNi_xCo_{1-x}O₂ thin films prepared by pulsed laser deposition. *Journal of Optoelectronics and Advanced Materials*, **12(12)** 2433-2436.
- M.C. Rao, Sk. Muntaz Begum, O.M. Hussain (2012).** Electrical conduction behavior of LiNi_xCo_{1-x}O₂ thin films. *AIP Conference Proceedings*, **1447(1)** 613-614.
- M.C. Rao, K. Ravindranadh, M.S. Shekhawat (2013).** Synthesis and applications of CdSe nanoparticles. *AIP Conference Proceedings*, **1536** 215-216.
- M.C. Rao (2013).** Pulsed Laser Deposition - Ablation Mechanism and Applications. *International Journal of Modern Physics: Conference Series*, **22** 355-360.

M.C. Rao, K. Ramachandra Rao (2014). Thermal Evaporated V_2O_5 Thin Films: Thermodynamic properties. *International Journal of ChemTech Research*, **6(7)** 3931-3934.

M.C. Rao, R.V.S.S.N. Ravikumar, K. Ravindranadh (2015). Structural and photoluminescence studies of Co^{2+} doped Ca–Li hydroxyapatite nanopowders. *Journal of Materials Science: Materials in Electronics*, **26** 6667–6675.

P.V. Prasad, K. Ramachandra Rao, M.C. Rao (2015). Structural and Photoluminescence Studies of Eu^{3+} doped L-Tartaric Single Crystal through Evaporation Technique. *Journal of Molecular Structure*, **1085** 115-120.

M.C. Rao et al., (2017). Structural and Optical Characterization of Organic Light Emitting Diodes. *Rasayanana Journal of Chemistry*, **10(1)** 298-304.

K. Lakshmi, M.C. Rao (2017). Optical and Photo luminescent Studies on VO^{2+} Doped SnO_2 Thin Films. *Rasayana Journal of Chemistry*, **10(2)** 682-688.

M.C. Rao, G. Ravi Kumar (2019). Influence of TiO_2 on structural, luminescent and conductivity investigations of CaF_2 – CaO – Y_2O_3 – B_2O_3 – P_2O_5 glasses. *Optik*, **179** 1109-1117.

M. Tejaswi, P. Pardhasaradhi, B.T.P. Madhav, M.C. Rao, N. Krishna Mohan (2020). Spectroscopic studies on liquid crystalline n-hexyloxy-cyanobiphenyl with dispersed citrate-capped gold nanoparticles in visible region. *Liquid Crystals*, **47(6)** 918-938.

B.T.P. Madhav, B. Prudhvi Nadh, T. Anilkumar, P. Pardhasaradhi, M.C. Rao (2020). Frequency reconfigurable split ring antenna for LTE and WiMAX applications. *International Journal of Electronics and Telecommunications*, **66(2)** 255-260.

R. Koutavarapu, M.R. Tamtam, S.G. Lee, M.C. Rao, D.Y. Lee, J. Shim (2021). Synthesis of 2D $NiFe_2O_4$ nanoplates/2D Bi_2WO_6 nanoflakes heterostructure: an enhanced Z-scheme charge transfer and separation for visible-light-driven photocatalytic degradation. *Journal of Environmental Chemical Engineering*, **9(5)** 105893.

R. Koutavarapu, M.R. Tamtam, M.C. Rao, J. Shim (2021). Enhanced solar-light-driven photocatalytic properties of novel Z-scheme binary $BiPO_4$ nanorods anchored onto $NiFe_2O_4$ nanoplates: Efficient removal of toxic organic pollutants. *Journal of Environmental Sciences*, **102** 326-340.

H.J. Kim, Y.G. Kang, H.G. Park, K.M. Lee, S. Yang, H.Y. Jung, D.S. Seo (2011). Effects of the dispersion of zirconium dioxide nanoparticles on high performance electro-optic properties in liquid crystal devices, *Journal of Liquid Crystals*, **38(7)** 871-875.