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Nanomaterials doping effects on blue phase liquid crystals

K.Indira[a], M. Santhosh[b] and T. Chitravel[c]

[a]Department of Physics, Pandian Saraswathi Yadav Engineering College, Sivagangai.

[b]Department of Physics, Arasu College of Engineering, Kumbakonam.

[c]Department of Physics, Anna University, Chennai, Madurai Region, Madurai.

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ABSTRACT

Liquid crystals are the soft materials composed of self organized molecules. They are known for their order and mobility which makes them a potential candidate for different applications. Among the different mesophases known, Blue phases are a special type of chiral nematic phases and some of them are optically isotropic. Generally these phases will be exhibited by molecules which possess sufficiently high anisotropy. These blue phases are usually stable for very narrow temperature range between the isotropic and the cholesteric phase. In the present work we will be studying the mesophase behaviour of liquid crystalline compounds doped with some chiral materials in different proportions to induce blue phase mesomorphism. The mesomorphic behaviour of these mixtures will be characterized using POM and DSC. Using ZnS Nanoparticles dispersed in these systems, we aim to widen the temperature range of the blue phase. Recently these nanomaterials stabilized blue phases are shown to have some advantages for display applications and is being actively studied across the world.

Introduction

Broadly, liquid crystals can be classified into (1) Thermo tropic Liquid Crystals - which are obtained by the action of heat on certain pure compounds or their mixtures and (2) Lyotropic Liquid Crystals - which are generated by the action of a solvent on suitable substrates. In this thesis, we are concerned with thermo tropic liquid crystals and excellent reviews are available on this topic, particularly those concerning calamitic and discotic liquid crystals. Blue phases can exist between the chiral nematic phase and the isotropic liquid phase of liquid crystalline materials with high chirality. They usually exist over only a very narrow temperature range (approximately 0.5 to 2 degrees C), although recent work at CMMPE has demonstrated blue phase materials with much wider temperature stabilities. There are three types of blue phase: BP I*, BP II* and BP III*, in order of appearance when heating towards the isotropic state. The three blue phases differ in the amount of order they possess and the structures that the chiral molecules form. Blue phases occur because the helicoidal structure of the chiral nematic phase is not the lowest energy configuration for chiral molecules. In the chiral nematic, molecules lie in quasi-nematic layers and rotate when going from one layer to the next. However, the free energy is actually lower if the molecules twist in two dimensions simultaneously. This leads to the formation of the double twist cylinder, where the molecules all rotate about a central axis.

Experimental methods:

Synthesis of ZnS Nanoparticles:

Nanosized inorganic Semiconducting materials have been generating an extensive interest in recent years, chemical and physical properties, which are different from those of the bulk materials. ZnS has a wide band gap of 3.5- 3.8 eV at room temperature and the band gap can be tuned in the UV region. It's an important inorganic material for a variety of applications including Photoconductors, solar cells, field effect transistors, sensors and display applications also. It has been investigated extensively, because of its potential optical applications. ZnS Doped with Various blue phase liquid crystal mixtures such as widen the blue phase temperature range. Nanostructured materials have been synthesized by many simple methods such as wet chemical method, solid state reaction method, etc. The purpose of the present work is to synthesize ZnS Nanoparticles using chemical method and doping the blue phase liquid crystal widen the blue phase temperature range.

The synthesis of ZnS Nanoparticles was carried out by aqueous chemical method using zinc chloride and sodium sulfide as source materials. All the reagents were of analytical grade and used without further purification. The entire process was carried out in distilled water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at low temperature and ambient conditions. In a typical preparation, solution of 1M Zinc chloride was prepared in 100 ml of deionized water and then the solution of 1M sodium sulfide was added drop by drop to the solution which was kept on stirring using a magnetic stirrer at 70^{o}C, which resulted in formation of ZnS nano colloid. The Nanoparticles were collected by centrifugation at 2000 rpm for 15 minutes. And further purification was made by ultrasonic bath. The resultant product was finally dried at 120^{o}C for 2 hours.

Preparation of liquid crystal mixtures:

The ROTN404 (Non-chiral) Liquid crystal and Cholesteryl nonanoate (non-Chiral) liquid crystal. The Cholesteryl Nonanoate has supplied by Thermax Company. The ROTN404 exhibits Nematic Phase only. But the Cholesteryl nonanoate pure sample exhibits smectic, cholesteric phases. But pure Cholesteryl nonanoate supplied by Thermax shows Blue phase (BP*). The ROTN404 and Cholesteryl nonanoate mixtures were prepared in different concentrations such as 60:40, 70:30 and

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80:20. The Mixture of 70:30concentration shows small range of Blue Phase. But the other concentration doesn't show Blue Phase as well as Smectic Phase. All the other concentrations show Cholesteric phase only.

In present study, ZnS Nanoparticles have been used to widen the Blue Phase temperature range. Details on their preparations and physical characterizations have been described. The so-produced ZnS Nanoparticles are essentially homogenously dispersed and have an average diameter of 32nm. The particle size is measured using powder X-ray diffraction method. The Optical properties are studied using UV-Vis Spectroscopy. The morphology of the Semiconductor nanomaterials as well as nanocrystalline size was investigated by Scanning Electron Microscopy.

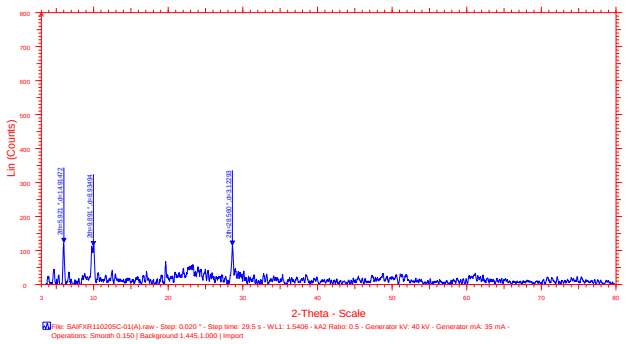
We made 60:40 concentration of ROTN404 and CN doped with ZnS Semiconducting nanomaterials. The mixture homogenously mixed at 45 minutes under isotropic temperature. The samples have been carefully checked under polarized optical microscopy.

Characterization

XRD diffraction studies of of ZnS Nanoparticles

Fig.2.1 shows the XRD patterns of the ZnS Nanoparticles. It reveals the hexagonal structure for the prepared Nanoparticles and the features correspond to (101), (002) and (110) planes, which shows obvious size broadening effects, indicating the finite size of the Nanoparticles.

A



The average particle size from the most intense peak was estimated to be 12 nm using Debye - Scherrer formula.

$$D = k\lambda/\beta\cos\theta \quad (1)$$

Where, D is the mean grain size, k is a geometric factor, λ is the X-ray wavelength, β is the FWHM of diffraction peak and θ is the diffraction angle. The FWHM of the XRD peaks may also contain contributions from lattice strain. The average strain of the ZnS Nanoparticles was calculated by Stokes – Wilson equation,

$$\varepsilon str = \beta/ 4\tan\theta \quad (2)$$

Lattice parameters 'a' and 'c' were calculated by the relation

$$d2/a2 = (h2+k2+l2)$$

$$d2/c2 = (h2+k2+l2) \quad (3)$$

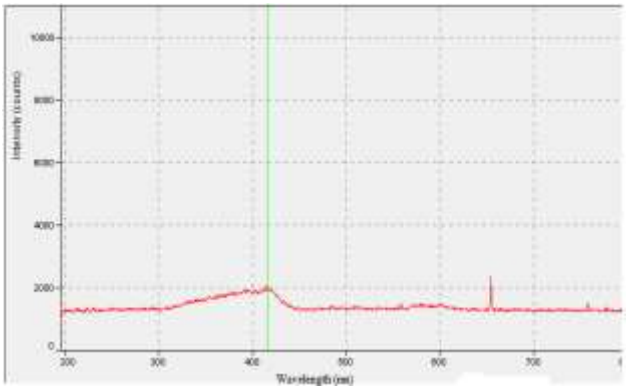
The dislocation density was also calculated from the relation

$$\delta = 15\ \varepsilon\ /aD \quad (4)$$

The average lattice strain and the dislocation density were estimated to be 2.80 x 10^{-3} and 3.39 x 10^{-15} lines/m.

UV-Vis Spectrum of the ZnS Np's:

The UV-Vis spectrum was recorded using Ocean Optics spectroscopy in the absorption mode and shown in fig 2.2



It exhibits the absorption edge of ZnS Nanoparticles at 418 nm (3.8 eV), which is slightly blue shifted from that of bulk ZnS (340nm, Eg = 3.65 eV). This closeness of the absorption peak to the bulk ZnS crystals are attributed to the near-band edge free excitation. The broadening of the absorption spectrum could be due to the quantum confinements of the Nanoparticles.

Blue Phase in Liquid Crystal Mixtures with 2% of ZnS Np's:

In the next part of work, stabilization of the ROTN404 and CN (Thermax Company) mixture was carried out using Zinc sulfide (ZnS). In the actual method, 98% ROTN404 + CN mixture and 2% ZnS was prepared by heating the mixture till they reach the isotropic phase. Once ready, the mixture was mounted on a glass slide and observed under Polarizing Optical Microscope for various phase transition by subjecting to heating and cooling cycle. Both blue phase and cholesteric phase were observed over wide range and at room temperature.

ROTN404 and CN 60:40 With 2% ZnS Mixture:

On Heating:

Figure 5.2.4(a) shows POM texture of the mixture 60% of ROTN 404 and 40% of CN(A) liquid crystals mixture doped with 2% ZnS Nanoparticles. This concentration mixture does not exhibit Smectic Phase.

Cho $\xrightarrow{94.5^oC}$ Blue Phase 95.7°C Iso

In this mixture exhibits small range of Blue Phase on heating (1.2-2.1°C). The values are tabulated in table

(HEATING) →

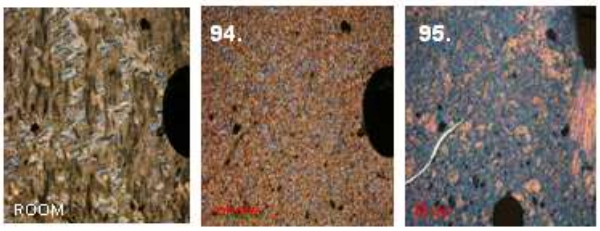


Figure 3.1(a). Texture of LC mixture under POM

On Heating Sample

S.NO	DATE	SAMPLE NAME	BLUE PHASE (°C)		ISOTROPIC TEMPERATURE (°C)		OTHER PHASES (°C)	COMPLETE BLUE STABLE TEMP (°C)
			START	END	START	COMPLETE		
1	16.3.11	nAa	94.5	95.7	95.7	Above	1).Cholesteric room temp to 94.5.	1.3
2	16.3.11	nAa	94.3	95.7	95.7	Above	1).Cholesteric room temp to 94.3.	1.5
3	16.3.11	nAa	93.2	95.3	95.3	Above	1).Cholesteric room temp to 93.2.	2.1

On Cooling:

The heating cycle showed blue phase that appeared in a range of 2-3^{0}C and the cooling cycle showed blue phase over a range of 3.5-5.6^{0}C. Hence we can conclude that incorporation of ZnS into the liquid crystalline matrix stabilizes the Blue phase and cholesteric phase over a wide range. Figure (3.1(b)).

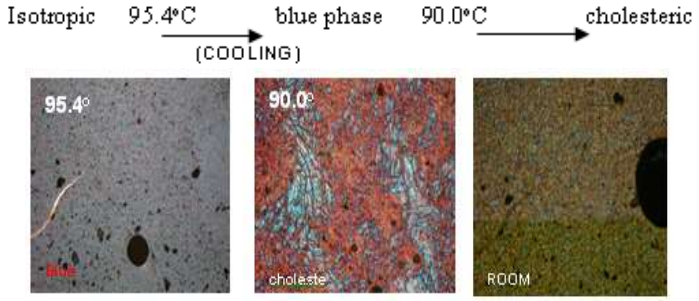


Figure 3.1(b) Texture of LC mixture under POM

On Cooling Sample:

s.no	sample name	blue phase (^{O}C)		isotropic temperature (^{O}C)	other phase (^{O}C)	BLUE TEMP RANGE (^{O}C)
		START	END			
1	nAa	93.7	90.8	93.7 Above	1).Cholesteric 90.8 to room temp onwards.	3.1
2	nAa	94.1	89.6	94.1 Above	1).Cholesteric 89.6 to room temp onwards.	4.5
3	nAa	95.4	90.0	95.4 Above	1).Cholesteric 90.0 to room temp onwards.	5.4

Conclusion

In the present experiment, synthesis of ZnS-Nanoparticles was carried out by aqueous chemical method and the particle size was characterized using XRD. UV-Vis Spectroscopy measured Optical Absorption. The liquid crystalline mixtures exhibiting Blue Phase over a narrow temperature range without doping where prepared. The temperature range of the blue phase in the liquid crystalline mixture were extended by doping of ZnS Semiconducting Nanoparticles. The stabilization of the Blue phase over a wide range after doping with ZnS-Nanoparticles was confirmed by observation under the Polarizing Optical Microscope. The main aim of stabilization of the blue phase over a wide temperature range and at room temperature can have potential application in liquid crystal displays.

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