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Citrate Capped Silver Nanoparticles Based Liquid Crystals-Spectroscopic Characterization.

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ABSTRACT

The synthesis and characterization on liquid crystalline (LC) *p*-undecyloxy benzoic acid (11OBA) with 30 µl citrate capped silver (Ag) nanoparticles dispersion are carried out. Spectroscopic techniques like X-ray diffraction spectrometric studies (XRD), scanning electron microscopy (SEM), Fourier Transform Infra Red Spectroscopy (FTIR), Ultra Violet Spectroscopy (UV) and differential scanning calorimetry (DSC) were performed on to the prepared samples. Textural determinations of the synthesized compounds are recorded by using polarizing optical microscope (POM) attached with a hot stage and camera. These results showed that the dispersion of citrate capped Ag nanoparticles in 11OBA exhibit nematic (NC) phases as same as the pure LCs, with reduced clearing temperature as expected. The smectic-C (SmC) thermal ranges are enhanced and the nematic thermal ranges are changed slightly both in DSC and POM with the dispersion of 30 µl citrate capped Ag nanoparticles.

Keywords: Synthesis, POM, DSC, Nano dispersion, XRD and SEM

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INTRODUCTION

Liquid crystals are self-assembled functional soft materials which possess both order and mobility at molecular, supra-molecular and macroscopic levels [1-3]. Liquid crystals are attractive materials, since they show unique properties, such as long-range order, cooperative effects and an anisotropic nature in optical and electronic properties, based on a self organizing nature in a certain temperature range with fluidity [4]. Owing to the possible synergetic relationship with nanomaterials, liquid crystals can play a very significant role in nanoscience and nanotechnology. Nanoparticles can be utilized to regulate and organize liquid crystal molecules in a systematic manner to achieve different phase manner under optimum environmental conditions. Nanoscale particles do not induce significant distortion of LC phases. Therefore, different nanomaterials are dispersed and studied in LC media to enhance the physical properties of LCs [5]. Moreover, alignment and self assembly of nanomaterials themselves can be achieved in LC phases [6]. The key point for all the possible applications is the alignment of liquid crystal molecules (i.e. the director) on the substrate [7, 8]. LCs act as tunable solvents for the dispersion of nanomaterials and LCs being anisotropic media, they provide a very good support for the self assembly of nanomaterials in to large organized structures in multiple dimensions. Hence LC mediated self assembly can be efficiently used to organize different kinds of nanomaterials in to soft and well defined functional super structures. Nano-objects (guests) that are embedded in the liquid crystals (hosts) can trap ions, which decrease the ion concentration and electrical conductivity and improve the electro-optical response of the host [10].

The properties of these nanoparticles are strongly determined by the characteristics of the noble metal core, such as its size and shape and the nature of the organic shell, which primarily serves to prevent aggregation of the metal nanocrystals. Diverse range of small-molecules and polymers with appropriate functional group(s) has been employed to stabilize the metal nanocrystals prepared by a variety of chemical reactions [10-12]. Among the inorganic nanomaterials, gold and silver nanoparticles have received great attention because of their unique electrical and optical properties, as well as their extensive applications in biomedical areas [13].

Silver nanoparticles have recently been shown to be a promising antimicrobial material [14]. Despite considerable success in synthesizing Ag nanoparticles with different dimensions and size ranges, many of the reported methods have certain limitations in terms of their control over shape, size and stability in the dispersion system [15]. On the other hand, the weaker reducing agent trisodium citrate (TSC) contributes to the formation of relatively large silver nanoparticles, having a wider size distribution. It can also result in a variation in the shape of the nanoparticles i.e. spherical nanoparticles are accompanied with undesired generation of rods, cubes and triangles [16, 17]. Samsung has created and marketed a material called Silver nano that includes silver nanoparticles on the surfaces of household appliances [18]. Rao et al. have presented the results on different oxide materials in their earlier studies [19-31]. In the present work citrate capped Ag nanoparticles are synthesized and dispersed in p-n-undecyloxy benzoic acids in different proportions and observed the variations in nematic range of liquid crystalline compounds.

EXPERIMENTAL

Synthesis of Citrate capped Ag nanoparticles

LC compound such as 11OBA, Silver nitrate ($AgNO_3$) and trisodium citrate dehydrate ($Na_3C_6H_5O_7 \bullet 2H_2O$) 99 % trisodium citrate, Silver nitrate are brought from Sigma-Aldrich laboratories, USA and used as such. Citrate capped Ag nanoparticles are synthesized in the laboratory from the citrate reduction process. First, 50 ml of 10 mM of Silver Nitrate is heated and 5 ml of 1 % trisodium citrate is added drop by drop and stirred vigorously for two hours. Then the solution changed gradually to pale yellow color indicates the formation of citrate capped Ag nanoparticles. The citrate capped Ag nanoparticles synthesized by this manner as citrate served the dual purpose of being the reducing agent as well as stabilizer.

Dispersion of nanoparticles into LC compounds

For uniform dispersion of nanoparticles in LCs, the nanoparticles are first dissolved in ethyl alcohol, stirred well about 45 minutes and later introduced in the isotropic state of mesogenic material (11OBA) in

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quantity 30 µl. After cooling, the nanocomposite 11OBA is subjected to study of the textural and phase transition temperatures using a polarizing optical microscope (SDTECHS make) with a hot stage in which the substance was filled in planar arrangement in 4 µm cells and these could be placed along with the thermometer described by Gray [32]. Textural and phase transition temperatures are studied after preparation of the sample and observations are made again to understand the stability of nanoparticles. A differential scanning calorimeter (Perkin Elmer Diamond DSC) is used to obtain the transition temperatures and the enthalpy values. XRD technique is used to determine the size of the citrate capped Ag nanoparticles which are dispersed in 11OBA. The presence of citrate capped Ag nanoparticles in 11OBA is studied by SEM data and existence as well as size is determined by XRD technique.

RESULTS AND DISCUSSIONS

POM Textures

The transition temperatures and textures observed by Polarizing Microscope in pure 11OBA are shown in Figure-1(a-d) while that of 11OBA with dispersed 30 µl citrate capped Ag nanoparticles shown in Figure-2(a-d) respectively. The results show that the dispersion of citrate capped Ag nanoparticles in 11OBA exhibits NC phases as same as the pure LCs, with reduced clearing temperature as expected. The SmC thermal ranges are enhanced and the nematic thermal ranges are changed slightly both in DSC and POM with the dispersion of 30 µl citrate capped Ag nanoparticles. The thermal ranges of nematic and SmC phases are changed slightly due to the dispersion of nanoparticles and the textures of the phase's changes by the self assembly of nanoparticles. The DSC thermograms are shown in the Figure-3 and Figure-4. The transition temperatures and enthalpy changes at the phase transformations determined through POM and DSC as shown in the Table-1.

Table 1: Phase variants, transition temperatures, Enthalpy values of 11OBA pure and with dispersed 30 µl citrate capped Ag nanoparticles

S.No	Compound	DSC/POM	Heating /Cooling	Scan Rate	Transition Temperatures °C				
					Solid-SmC	SmC-N	N-I	SmC thermal range °C	Nematic Thermal range °C
1	11OBA PURE	DSC	Heating	20° c/min	99.09	129.24	140.58	29.15	11.34
		POM	Heating		98.5	129.8	140.4	31.3	10.6
2	11OBA +30 µl ct capped Ag	DSC	Heating	20° c/min	96.0	129.41	140.23	33.41	10.82
		POM	Heating		94.4	128.0	139.4	33.6	11.4

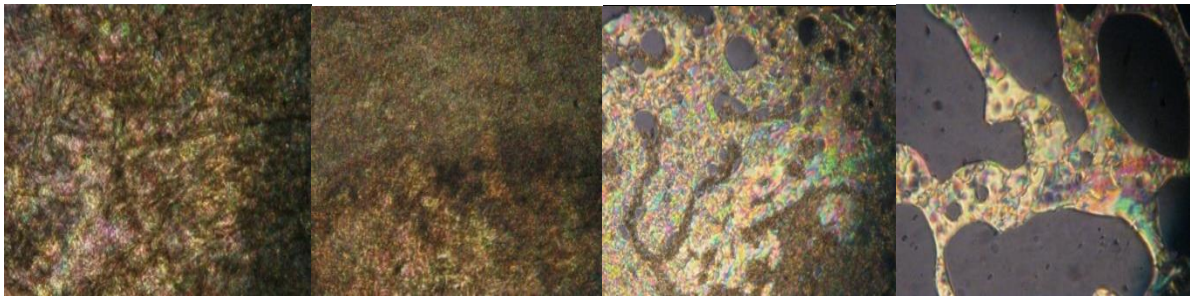

Figure 1a: Solid at 85.5 °C **Figure1b: Solid-Smectic C at 90.5 °C** **Figure1c: Smectic-Nematic at 127.8 °C** **Figure1d: Nematic - Isotropic at 138.9 °C**

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11OBA + 30 µl ct capped Ag nanoparticles

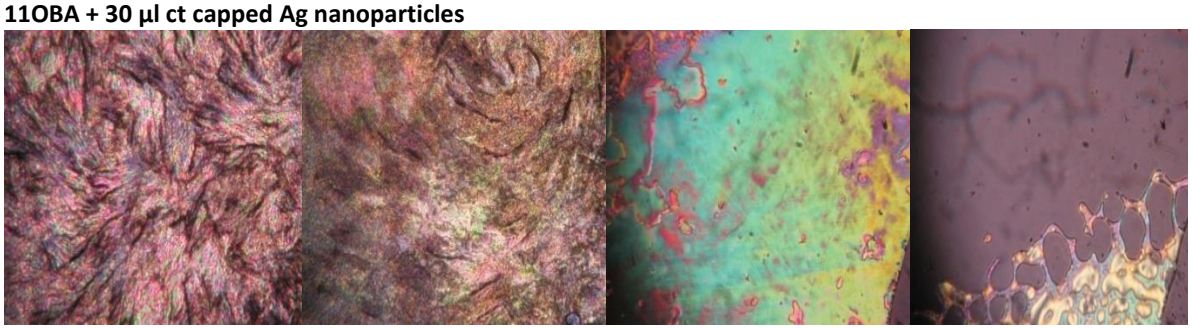

Figure 2a: Solid at 90.5 ^{0}C **Figure 2b: Solid-Smectic C at 94.4 ^{0}C** **Figure 2c: Smectic-Nematic at 129 ^{0}C** **Figure 2d: Nematic - Isotropic at 141.4 ^{0}C**

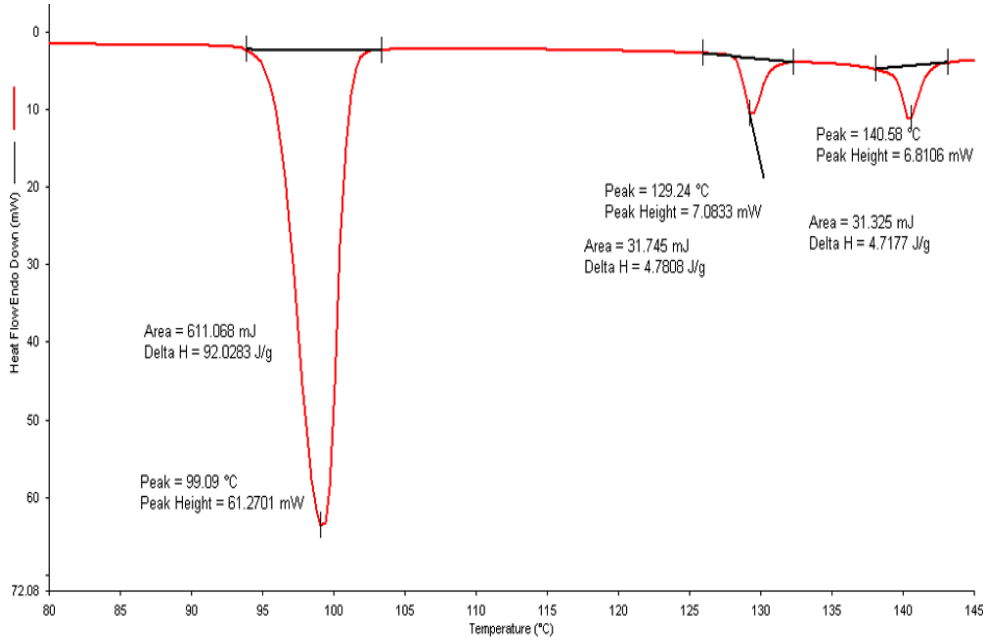

Figure 3: DSC thermogram of 11OBA pure compound

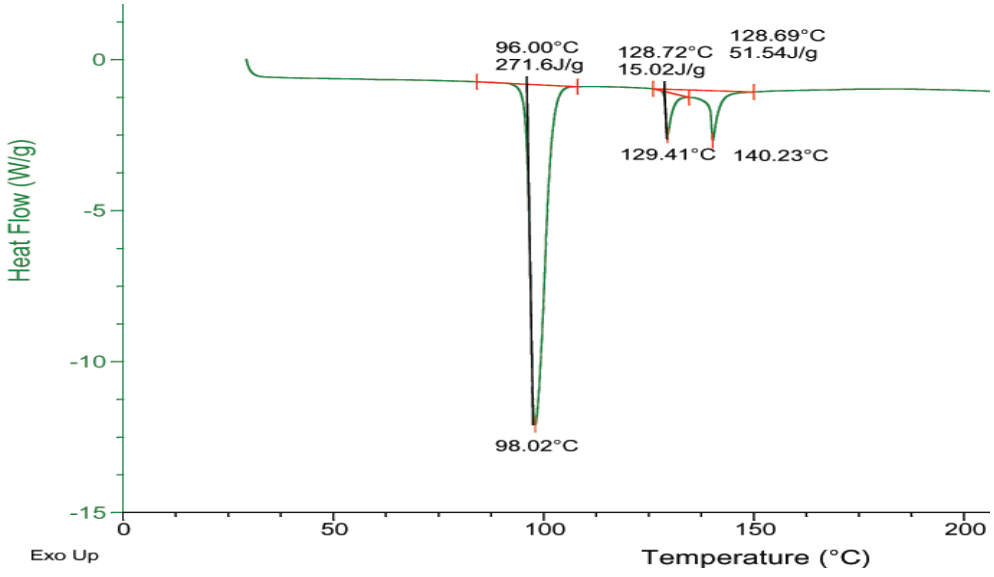

Figure 4: DSC thermogram of 11OBA with dispersed 30 µl citrate capped Ag nanoparticles

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Ultraviolet –Visible (UV) Spectroscopic Studies

The Figure-5 shows the UV-visible spectra of 11OBA pure, pure citrate capped Ag nanoparticles and citrate capped Ag nanoparticles dispersed in 11OBA LC sample. It is observed that the spectrum for pure 11OBA does not exhibit any absorption peaks in the wavelength range 400 – 450 nm. However, the spectrum of nanodoped 11OBA shows the significant peak at 406 nm, which is the characteristic peak of citrate capped Ag nanoparticles. The decrease of absorbance peak in 11OBA with the dispersion of citrate capped Ag nanoparticles resembles the capping of nanoparticles with 11OBA. So, the UV-visible spectral study confirms the presence of citrate capped Ag nanoparticles in 11OBA.

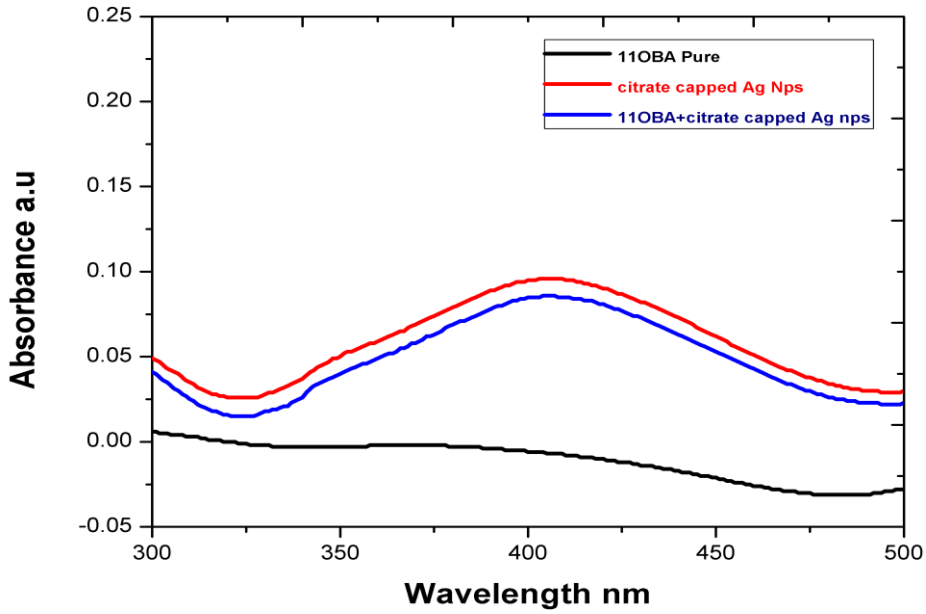

Figure 5: UV-visible spectra of 11OBA with dispersed 30 µl citrate capped Ag nanoparticles

FTIR Studies

FTIR is used to analyze presence of functional groups in molecule and presence of dopants is represented by the change in the transmittance as shown in the spectrum. As synthesized citrate capped Ag nanoparticles dispersed in 11OBA compound is analyzed by using FTIR at room temperature. The compound is stable at room temperature, so a small amount of compound is taken directly for the spectral recording by using ATR (Attenuated Total Reflectance) technique and the IR frequencies in solid state which are correlated in bond with the pure bond 11OBA. The assigned bonds corresponding to the resultant frequencies from the spectra are tabulated. Due to the excitation of both molecular vibrations and rotations absorptions of electromagnetic radiation causes the formation of absorption bands in the IR spectra which are useful to explain the bonding interaction of the molecules. In both spectra exhibit a strong electromagnetic absorption at 1577.98 cm^{-1} , 1605.99 cm^{-1} and 1248.10 cm^{-1}, 1241.09 cm^{-1} corresponding to aromatic ring stretching. The absorption band at 2912.31 cm^{-1} and 2919.31 cm^{-1} correspond to OH bond. The existence of OH bond vibration at 637.34 cm^{-1}, 631.35 cm^{-1} and also represents the benzoic acids moiety due to their strong intensity and strongly supports the existence of 11OBA. The bond 826.4 cm^{-1}, 847.41 cm^{-1} are assigned to stretching ring vibration at the out of plane [33]. While dispersing the citrate capped Ag nanoparticles the intensity of the peaks are found to be decreased as shown in the Figure-6. The intensity of 11OBAwith dispersed nanoparticles is found be decreases, this related to the change in dipole that occurs during the vibration. The vibrations that produce small change in dipole result in a less intense absorption than those that result in a relatively modest change in dipole (Table-2). As we have taken the FTIR data in mid infra red region, it is not possible to take the nanoparticle data.

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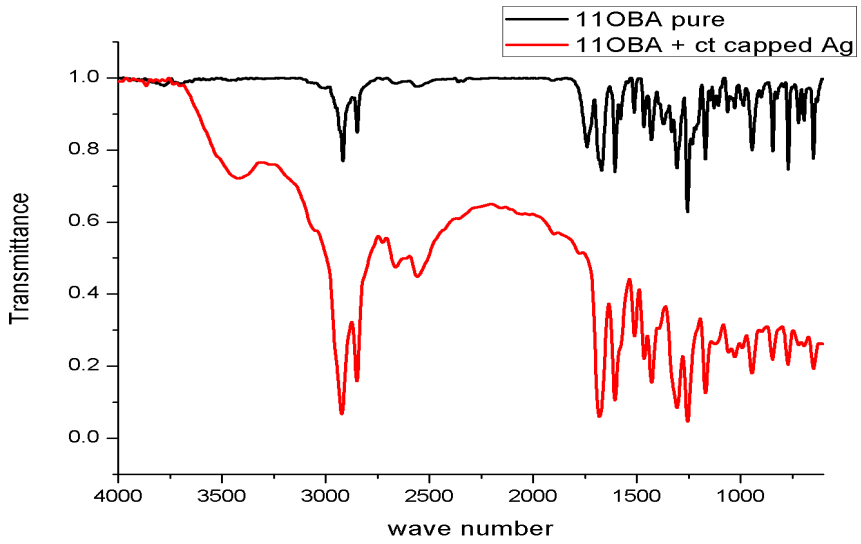

Figure 6: FTIR of 11OBA pure and with 30 µl citrate capped Ag nanoparticles

Table 2: Functional group intensities for 11OBA pure and with dispersed citrate capped Ag nanoparticles across the following wavelengths

S.No	Wavelength cm^{-1}	Intensity for pure LC	Intensity for LC with dispersed citrate capped Ag nanoparticles	Functional Group
1	2912.31	0.7759	0.1062	OH bond
2	1662.01	0.7636	0.0687	Benzoic acid
3	1577.98	0.7481	0.1432	Ring stretching
4	1500.96	0.9494	0.3137	
5	1458.94	0.9	0.3137	
6	1423.15	0.8597	0.1816	
7	1248.1	0.6642	0.0501	Aromatic ring
8	1149.29	0.7852	0.1618	CHOH bending vibration
9	953.22	0.8285	0.1896	Ring out of plane
10	826.4	0.8009	0.2487	
11	749.38	0.7604	0.2302	Aromatic ring
12	637.34	0.7883	0.2054	OH bond

SEM Studies

A small amount of citrate capped Ag nanoparticles and nanoparticles dispersed LC compounds are taken on sample holder for the scanning electron microscopy. The SEM provides the investigator with a highly magnified image of the surface of a material as the present sample contains electrons; which are needed for getting SEM image. The resolution of the SEM can approach a few nm and it can operate at magnifications that are easily adjusted from about 10×-300,000×. SEM gives not only topographical information but also gives the information regarding the composition of the elements in the material [34]. The SEM images of citrate capped Ag nanoparticles and with the dispersion of 30 µl citrate capped Ag nanoparticle in 11OBA is shown in the

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Figure-7 and Figure-8. It is clear from Figure 8 that the nanoparticles are in the size of approximately 70 nm. From EDS data shown in Figure-7 elucidates the presence of nanoparticles in the compound is well established.

Element	Weight %	Atomic %
C K	71.18	76.61
O K	28.97	23.40
Ag L	-0.15	-0.02

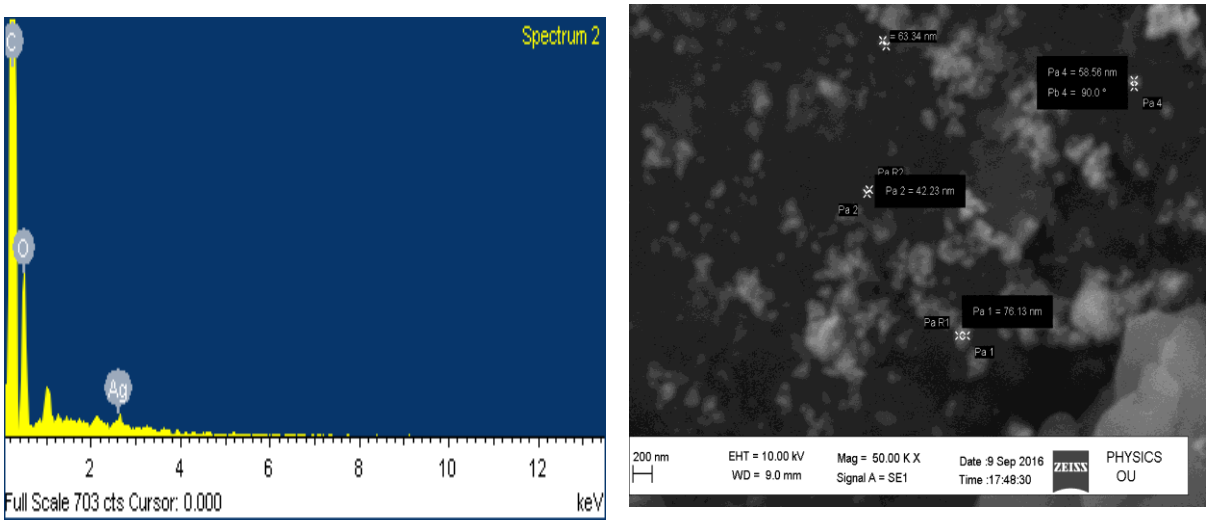

Figure 7: EDS data of 11OBA with dispersed citrate capped Ag Nanoparticles

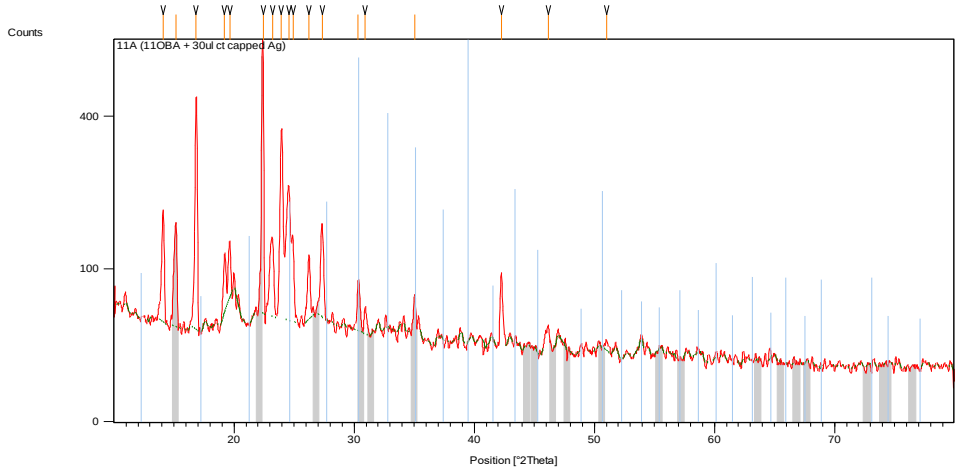

Figure 8: SEM Image

XRD Studies

The XRD data of 11OBA with w % of thiol capped Ag nanoparticles is shown in the Figure-9. In comparison of JCPDF data peaks were well resolved and are matched with JCPDF card no.00-023-1891which is clearly evidenced the existence of citrate capped Ag nanoparticles in 11OBA. By using Schrrer's Formula, $t = k\lambda/\beta\cos\theta$, grain size 65 nm, Λ=1.54 A^o, β= FWHM, Peaks at 15.17^0, 30.34^0, 35.03^0 also resembles the existence of citrate capped Ag nanoparticles dispersed in 11OBA.

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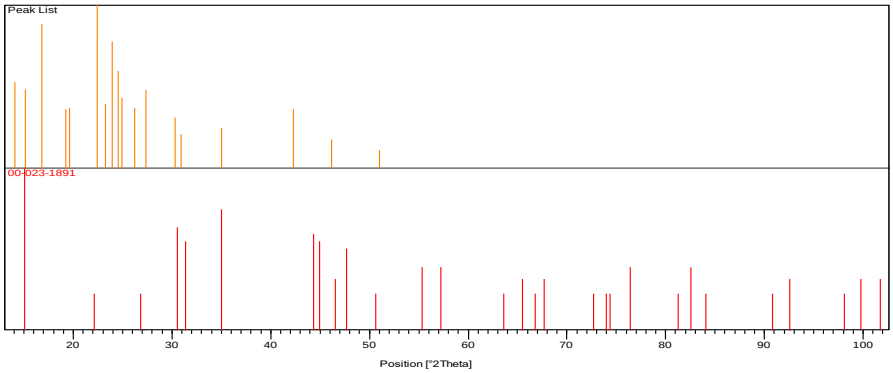

Figure 9: XRD of 11OBA with dispersed 30 µl citrate capped Ag nanoparticles

CONCLUSIONS

From these studies on 11OBA liquid crystal compound with dispersed citrate capped Ag nanoparticles, transition temperatures obtained from POM attached with the hot stage are in good agreement with those obtained from DSC. The slight differences can be attributed due to the different experimental conditions. The transition temperatures of nematic as well as smectic c phases has been reduced slightly while dispersing the ct capped Ag nanoparticles. The thermal ranges of nematic phase have been changed slightly while increased that of SmC with the dispersion of citrate capped Ag nanoparticles. From FTIRstudies, the intensity of 11OBA with dispersed citrate capped Ag nanoparticles is found to be decreased. This related to the change in dipole that occurs during the vibration. The presence of citrate capped Ag nanoparticles is evidenced from SEM and XRD studies. The size of the citrate capped Ag nanoparticles is found to be 65 nm from XRD studies and is agreed with the value obtained from SEM.

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