Journal of Molecular Liquids 268 (2018) 223–228

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Effects of manganese (II) titanium oxide nano particles on the physical properties of a room temperature nematic liquid crystal 4-(trans-4′-n-hexylcyclohexyl) isothiocyanatobenzene

Hajer H.M. Elkhalgi [a], Sarita Khandka [a], Neelam Yadav [b], Ravindra Dhar [b,*], R. Dabrowski [c]

[a] Department of Physics, Sam Higginbottom University of Agriculture, Technology and Sciences, Allahabad 211007, India
[b] Centre of Material Sciences, University of Allahabad, Allahabad 211002, India
[c] Institute of Applied Sciences and Chemistry, Military University of Technology, 00-908 Warsaw, Poland

A R T I C L E I N F O

Article history:
Received 9 May 2018
Received in revised form 7 July 2018
Accepted 11 July 2018
Available online xxxx

Keywords:
Liquid crystals
Nano particles
Thermodynamic
Threshold voltage
Dielectric anisotropy

A B S T R A C T

In the present work, Manganese (II) Titanium Oxide nanoparticles ($MnTiO_3$-NPs) were dispersed in a room temperature nematic liquid crystal 4-(trans-4′-n-hexylcyclohexyl) isothiocyanatobenzene (6CHBT) at the concentrations of 0.5 wt% and 1 wt% and their thermodynamic, optical and dielectric properties were investigated. Effects of dispersion of $MnTiO_3$-NPs on various electro-optical and display parameters of host liquid crystalline material have been studied. Physical parameters, such as threshold voltage, dielectric anisotropy and splay elastic constant have enhanced for composite systems. Due to the dispersion of $MnTiO_3$-NPs, nematic to isotropic transition temperature has increased for the composite systems.

1. Introduction

Liquid crystals (LCs) are anisotropic fluid which exhibits both the properties of liquid and solid. As its name suggests it is an intermediate phase of matter in between the liquid and crystal [1, 2]. The molecules in a crystal possess both positional and orientational order while the molecules in a liquid can move freely in random manner and do not have any order. Liquid crystals (LCs) emerge as a smart fluid for dispersion of nano structures (viz. nanoparticles, nanotubes, and quantum-dots) because of its anisotropic physical properties and elastic mediated interaction between medium and foreign objects which is promising for self-assembly of nanostructures. LCs are fascinating organic materials being unique in their properties such as directional anisotropy and fluidity like ordinary liquids [3] There has been much interest in the possible technological physics and applications of nanoparticles (NPs) suspended in LCs as a host. Since the beginning of the last decade the study of the influence of nano systems on the properties of liquid crystal has attracted considerable scientific interest [4, 5]. The electrical, optical, and magnetic properties of the LCs host can be altered by addition of nanostructures; these composites are very beneficial in devices based on LCs [6]. By the mutual interactions at molecular level and due to the similarity in dimensions, NPs share their intrinsic properties with LCs. Influence of nanoparticles, quantum dots or nanotubes on liquid crystalline properties is generally achieved by adding a very low concentration of nano entities into the LC matrix [7–9]. Composite materials consisting of LC dispersed with NPs have indeed attracted considerable technological and scientific interest, because the incorporation of NPs enhances the electro-optical properties of the LCs itself with ease of alignment of composites [10–29]. Although there are many studies for 6CHBT with different nano-structures [30–38] but reports on LCs doped with multiferroic NPs are rare. In the present work, we report a study on changes occurred in the display parameters, dielectric and optical properties of a room temperature nematic material 4-(trans-4′-n-hexylcyclohexyl) isothiocyanatobenzene (6CHBT) due to the dispersion of the Manganese (II) Titanium Oxide nano powder ($MnTiO_3$-NPs) having particle size of <50 nm. Multiferroic $MnTiO_3$ has good optical and electrical properties [39].

2. Experimental techniques

$MnTiO_3$-NPs have been dispersed in 6CHBT. 6CHBT was chosen as a host for dispersion of $MnTiO_3$-NPs because it possesses low viscosity and has a wide range of nematic phase (12.5 °C–42.3 °C) [31]. $MnTiO_3$-NPs with particle size <50 nm have been procured from Sigma-Aldrich and were used without further treatment. The LC–NPs composites were prepared by adding a small weight percentage of $MnTiO_3$-NPs (0.5% and 1%) in 6CHBT. Both the host LC material and NPs were weighed using a Shimadzu's semi-micro balance (AUW120D) and were mixed in the isotropic phase. The mixture was

* Corresponding author.
E-mail address: rdhar@allduniv.ac.in (R. Dhar).

https://doi.org/10.1016/j.molliq.2018.07.044
0167-7322/

ultrasonicated for 3 h in order to ensure proper mixing and homogeneous distribution of $MnTiO_3$-NPs in the LC material. A Polarized Light Microscope (PLM) was used to verify the homogeneous dispersion of $MnTiO_3$-NPs in LC matrix. Although such small NPs cannot be visualised directly under PLM but scattering of light around NPs show signature of their presence. Differential Scanning Calorimeter (DSC) of NETZSCH model DSC-200-F3-Maia was used to perform thermodynamic studies on the pure and dispersed samples. In order to stabilize the peak transition temperatures and corresponding enthalpy of composites, the DSC was initially allowed to run for first two cycles at a scan rate of 5 °C/min in the range from −20 °C to 60 °C. Peak transition temperatures (Tp) have been determined with the accuracy of 0.1 °C for fully-grown peaks. The pure and dispersed samples of $MnTiO_3$-NPs were filled in parallel plate capacitor type cells made of two overlapping indium tin oxide (ITO) coated glass electrodes with separation of 5 μm (make-Instec, USA) for electro-optical measurements. The ITO glass substrates were coated with polymer and rubbed anti-parallel in order to achieve planar alignment. The transmission intensity of white light has been measured by a photo-detector (made by Instec, USA) mounted on PLM and corresponding photo-voltage has been measured. Transmission-Voltage (T-V) curves have been plotted for pure LC and composites to determine the threshold voltage (V_T). These planar aligned cells have also been used to measure the transverse component of relative permittivity ($\varepsilon'_{\perp}$). However, to measure the longitudinal component of relative permittivity ($\varepsilon'_{\parallel}$), capacitor type cells made of overlapping ITO coated glass substrates treated for homeotropic alignment and separated by 9 μm spacer (make-Instec, USA) have been used. Impedance analyser (make-NOVOCONTROL TECHNOLOGIES) has been used to acquire dielectric data in the frequency range of 1 Hz–10 MHz. The pure LC and composites have been filled in the cells at temperatures, 10 °C above the isotropic to nematic transition temperature. The relative permittivity (ε'), dielectric loss (ε'') and other parameters have been obtained from the measured capacitance and conductance data of the cell filled with samples as described earlier under both planar and homeotropic alignment of molecules. The temperature of the samples for aforesaid measurements has been controlled with the help of a hot stage made by Instec (model HS-1).

The cells were calibrated and the active capacitances of the empty cells were determined in order to calculate the dielectric parameters (permittivity, loss and conductivity) of the materials from measured impedance data. The capacitance of the empty cell with air as medium between plates is given by:

$$C\,(a) = C_A + C_D \quad (1)$$

where, C_A and C_D are active and dead capacitances of the cell. By filling cyclohexane in the cell, C_A has been determined. The capacitance of the cell filled with cyclohexane is as follows:

$$C\,(ce) = \varepsilon'\,(ce)\,C_A + C_D \quad (2)$$

where ε' (ce) is the relative permittivity of cyclohexane at 30 °C.

Finally, the above two equations yield:

$$C_A = [C\,(ce) - C\,(a)]/[\varepsilon'\,(ce) - 1] \quad (3)$$

The permittivity (ε') and loss (ε'') of the material have been calculated with the help of the following equations:

$$\varepsilon' = [\{C\,(m) - C\,(a)\}/C_A] + 1 \quad (4)$$

and

$$\varepsilon'' = \sigma/\varepsilon_0\omega = 1/(2\,\pi\,f\,RC_A) \quad (5)$$

where C (m) is the capacitance of the cell filled with material; σ is the conductivity, f is the frequency; and R is the resistance of the material filled between parallel glass plates. The contribution of dead capacitance is neglected in the case of Instec cells as ITO is etched off in the area other than active portion. Permittivity is defined as.

$$\varepsilon' = C\,(m)/C_A \quad (6)$$

A Shimazdu ultraviolet-Visible (UV–Vis) spectrophotometer was used to obtain absorption spectra. For these measurements, cuvette of path length 10 mm was used and chloroform was used as a solvent.

3. Results and discussion

Fig. 1a and b illustrates a typical plot of heat flow with respect to temperature for pure, 0.5 wt% and 1 wt% $MnTiO_3$-NPs composites on heating and cooling at scan rate of 5.0 °C/min. The isotropic to nematic transition temperature (T_{IN}) increases by 0.2 °C for 0.5 wt% doped nanocomposite while cooling. Also, the area and height of the transition peak becomes larger than the transition peak obtained for pure 6CHBT. This shows that the ordering between the LC mesogens increases by addition of multiferroic NPs. Lopatina and Selinger [40] have given a model that predicts that the stabilization of the nematic phase occurs due to the interaction between the orientational distribution of the NP dipole moment and the orientational order of LCs; which is the cause for increase in T_{IN}. Li et al. [41] have demonstrated an increase in T_{IN}. The authors attributed it to the production of large local electric field by NPs, which polarized the LC molecules and in turn led to the increased intermolecular interaction. Pandey et al. [42] proposed the increase in the effective chain length of the molecules as the reason behind the increase in transition temperature.

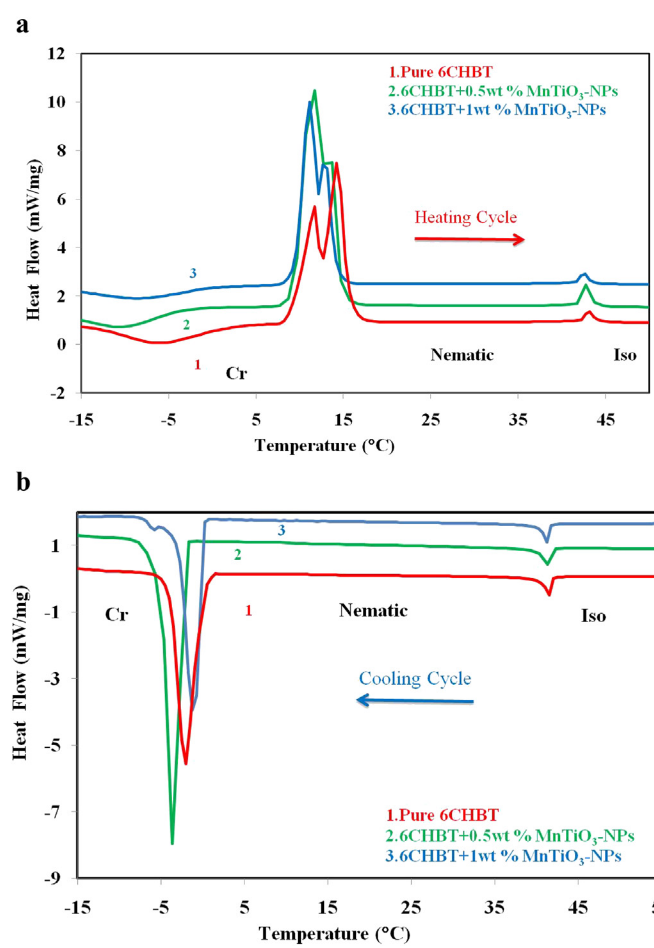

Fig. 1. DSC thermograms for the (a) heating and (b) cooling cycles at the scan rate of 5.0 °C/min.