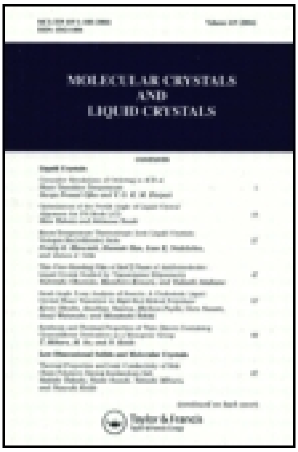

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Change in Dielectric and Electro-Optical Properties of a Nematic Material (6CHBT) Due to the Dispersion of $BaTiO_3$ Nanoparticles

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Change in Dielectric and Electro-Optical Properties of a Nematic Material (6CHBT) Due to the Dispersion of $BaTiO_3$ Nanoparticles

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Thermodynamical, dielectric and electro-optical studies of a ferroelectric nanopowder (0.5 weight% Barium Titanate, $BaTiO_3$) dispersed in 4-(trans-4-n-hexylcyclohexyl) isothiocyanatobenzoate (6CHBT) have been carried out. Change in the dielectric anisotropy, relaxation frequency and activation energy of an observed non-collective relaxation mode, threshold and switching voltages of electro-optic response (transmission-voltage characteristic) have been determined for the dispersed and pure samples in their nematic mesophases. These studies suggest that isotropic to nematic transition temperature for $BaTiO_3$ dispersed 6CHBT is lowered. Changes in other properties are also discussed.

Keywords Dielectric anisotropy; ferroelectric nanoparticles; nematic liquid crystals; transmission voltage characteristic

1. Introduction

In the past few years nano-systems have received significant attention of researchers because of their interesting physical properties [1–6]. Some researchers have tried to incorporate these properties into liquid crystals (LCs) by preparing liquid crystal-nano composites [7–14]. It has been shown that nematic matrix of LC can be used to align the Carbon Nanotubes (CNTs) [12]. Fenghua Li *et al.* have suggested that nano-colloids can be used to improve the performance of liquid crystal

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displays and related optical communication applications [11]. Reznikov *et al.* have reported that ferroelectric nanoparticles substantially lower the threshold voltage by enhancing the dielectric anisotropy of the LC materials and is sensitive to the sign of the applied electric field [13]. To understand the experimental results of ferroelectric nanoparticles in nematic liquid crystals, even a statistical theory has been developed [10]. This theory predicts the enhancement of the isotropic-nematic transition temperature due to the dispersion of ferroelectric nanoparticles in nematic liquid crystals. Doping a nematic LC with a small amount of ferroelectric nanoparticles strongly affects the dielectric properties of the system. The larger dielectric anisotropy in ferroelectric nematic suspension is caused by the permanent dipole moment and geometrical anisotropy of the ferroelectric nanoparticles [14].

4-(trans-4-n-hexylcyclohexyl) isothiocyanatobenzoate (6CHBT) is a basic display material and most of its physical properties have already been reported [15]. It possess nematic phase in the temperature range 12.0–43.0°C. In the present study, we have dispersed low concentration (~0.5 wt%) of ferroelectric nano-powder of $BaTiO_3$ in 6CHBT. Thereafter, we have investigated the temperature and frequency dependent relative dielectric permittivity and loss, relaxation frequency and activation energy of an observed relaxation mechanism along with the electro-optical parameters such as threshold voltage, switching voltage of the pure as well as nano system dispersed with liquid crystal.

2. Experimental Methods

The nano-composite (6CHBT + 0.5 wt% $BaTiO_3$) was prepared by dispersing $BaTiO_3$ nano-powder in pure 6CHBT. Purity of liquid crystalline material used in the present study was ~99%. The characteristic size of the ferroelectric nano particles in the composite was about 30–50 nm and the structure was isotropic polyhedron. Shimadzu's semi-micro balance (AUW120D) having an accuracy of 10 μg has been used to weigh appropriate weight of 6CHBT (177.5 mg) and $BaTiO_3$ (0.92 mg). Then both were mixed in the isotropic phase and ultrasonicated for 15 minutes to ensure homogeneous distribution of the particles. For the electro-optical work, Instec (USA) made dielectric cells (thickness 5 μm and pre-tilt 1–3°) have been used to get planar alignment of the sample. However, Instec cells are not appropriate for the dielectric studies as their frequency response deteriorates above 100 kHz due to high resistance of indium tin oxide (ITO) coated glass electrodes. Hence, for the dielectric work, our lab made cells with low resistance ITO and gold-coated glass plates as electrodes with proper surface treatment have been used [16]. Dielectric data have been acquired using a N4 L Phase Sensitive Multimeter (model PSM1735) in the frequency range of 1 Hz to 35 MHz [16,17]. To analyze the measured data, the dielectric spectra have been fitted with the generalized Cole–Cole equation [16–19] using origin software. The low [20] and high [21,22] frequency parasitic effects have been removed by the process of fitting [16,19]. Temperature of the sample has been controlled with the help of a hot stage from Instec (model HS-1). The other details of experimental techniques have been discussed in our earlier publications [16,17].

3. Results and Discussion

The thermodynamic parameters of the pure and dispersed 6CHBT were determined by the Differential Scanning Calorimeter (DSC) of NETZSCH (model DSC 200 F3, Maia). Initially, five heating and cooling scans were allowed to the pure and dispersed samples in order to stabilize their thermodynamic parameters and then different scans were carried out with scan rates from 2.5 K/min to 15.0 K/min. Figure 1 shows a typical plot of heat flow (mW/mg) with temperature (in°C) in the heating and cooling cycles at the scan rate of 5.0 K/min. for pure and dispersed samples. The phase transition temperatures of both pure and dispersed 6CHBT increase linearly with the scan rate as discussed earlier [23,24]. By using least square fit (LSF) of transition temperatures with scan rate, we have obtained the extrapolated transition temperatures at the scan rate of 0°C/min which is under thermal equilibrium [23,24]. Values of the transition temperatures thus obtained and transition enthalpies are given in Table 1. From the Table, it is evident that both, the transition temperatures and enthalpies of the pure 6CHBT are reduced due to dispersion of $BaTiO_3$ nanoparticles. We find that isotropic-nematic transition enthalpy of the dispersed sample decreases by 24% as compared to that of the pure 6CHBT sample.

Figure 2 shows the variation of the longitudinal ($\varepsilon'_{\parallel}$) and transverse ($\varepsilon'_{\perp}$) components of the relative dielectric permittivity (henceforth we will call it 'dielectric permittivity') which reflects dielectric anisotropy ($\Delta\varepsilon' = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$) as well with temperature for the pure and dispersed samples. Figure 2 show that dielectric anisotropy decreases due to dispersion of $BaTiO_3$ mainly because of the decrease in the longitudinal component of the dielectric permittivity. We find that $\Delta\varepsilon'$ of the dispersed sample decreases by 20% as compared to that of the pure 6CHBT sample. Ouskova *et al.* have reported increase in $\Delta\varepsilon'$ when submicron ferroelectric $Sn_2P_2S_6$ particles were dispersed in a nematic liquid crystal host (ZLI-4801-000) at a low volume concentration (0.3 wt%) [14]. However, Ouskova *et al.* have also observed small change in transverse component of the dielectric permittivity as compared to longitudinal component due to dispersion as observed by us. Maier and Meier theory [25,26] suggests that the dielectric anisotropy is proportional to the order parameter (S). From the thermodynamic and dielectric studies, we find that isotropic to

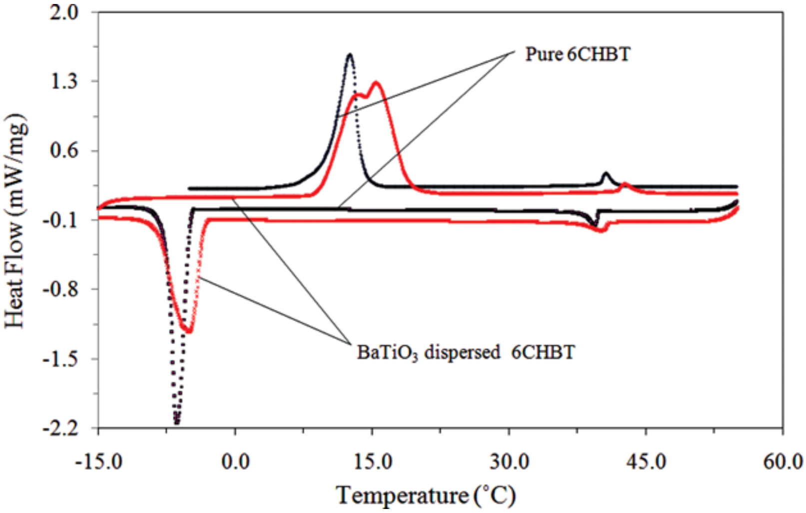

Figure 1. DSC thermograms for the heating and cooling cycles at the scan rate of 5.0 K/min for pure and $BaTiO_3$ dispersed 6CHBT. (Figure appears in color online.)

Table 1. Variation of the isotropic-nematic transition temperature T_{IN} (in°C), transition enthalpy (ΔH_{IN} in J/g), longitudinal ($\varepsilon'_{\parallel}$) and transverse components of the dielectric permittivity ($\varepsilon'_{\perp}$), dielectric anisotropy ($\Delta\varepsilon'$), ratio $\Delta\varepsilon'/\varepsilon'_{\perp}$, relaxation frequency ($f_R$ in MHz) and activation energy (E_A in kJ/mole) of an observed relaxation mode in the homeotropic aligned samples, threshold voltage (V_{th} in volt), and effective splay elastic constant (K_{11} in N) at 27.0°C

Sample (27.0°C)	T_{IN}	ΔH_{IN}	$\varepsilon'_{\parallel}$	$\varepsilon'_{\perp}$	$\Delta\varepsilon'$	$\Delta\varepsilon'/\varepsilon'_{\perp}$	E_A	f_R	V_{th}	$K_{11} \times 10^{-10}$
Pure 6CHBT	42.1[a] 41.7[b]	2.13	10.6	4.1	6.5	1.6	71	2.3	0.7	0.029
$BaTiO_3$ dispersed 6CHBT	41.6[a] 41.7[b]	1.62	9.1	3.9	5.2	1.3	68	2.4	1.3	0.079

[a]From dielectric studies, [b]From thermodynamics studies (DSC).

nematic transition temperature is decreasing for the dispersed sample as compared to that of the pure sample (see Fig. 1 and Table 1) which suggests decrease of S due to dispersion of $BaTiO_3$. Decrease of S seems responsible for the decrease of $\Delta\varepsilon'$ due to dispersion of $BaTiO_3$. There may be some other parameters also responsible for the decrease of $\Delta\varepsilon'$ e.g., change of the effective dipole moment (μ) of the molecules.

Transverse component of the dielectric permittivity remains invariant in the measured frequency range 1 kHz-10 MHz which suggests that there is no relaxation mechanism in the planar alignment of the molecules upto the highest measured frequency. However, we have observed a relaxation mode in the case of homeotropic alignment of the molecules. Figure 3 shows the variation of $\varepsilon'_{\parallel}$ and $\varepsilon''_{\parallel}$ with frequency. From the fitting of the measured data of $\varepsilon'_{\parallel}$ and $\varepsilon''_{\parallel}$ with the generalized Cole-Cole equation [17–19], we have determined dielectric strength ($\delta\varepsilon'_{\parallel}$), relaxation frequency

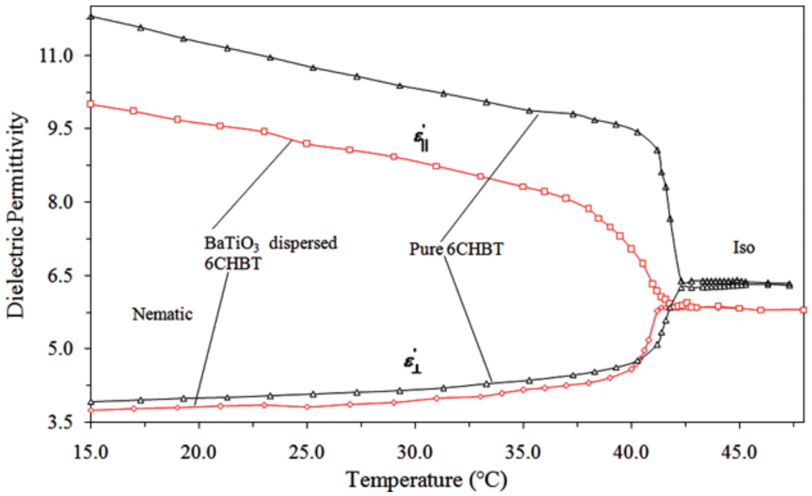

Figure 2. Temperature dependence of the longitudinal and transverse components of the dielectric permittivity for the pure and $BaTiO_3$ dispersed 6CHBT. (Figure appears in color online.)

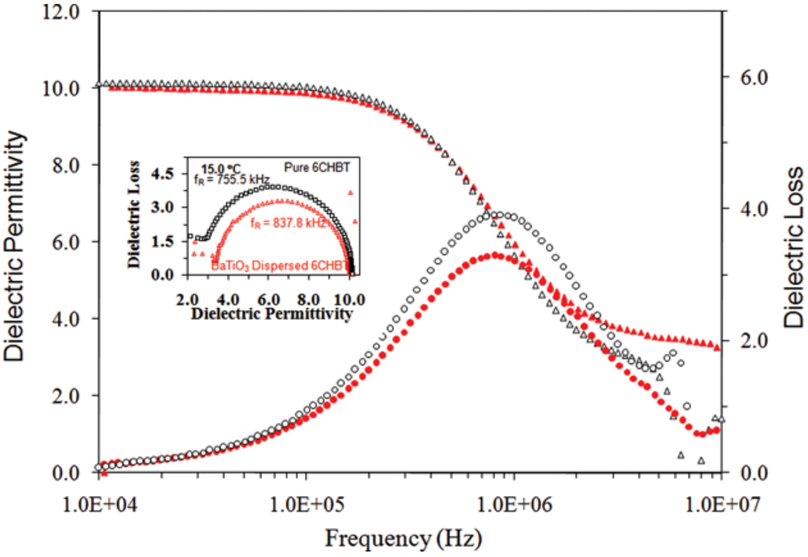

Figure 3. Frequency dependence of the corrected values of longitudinal component of the dielectric permittivity ($\varepsilon'_{\parallel}$) and loss ($\varepsilon''_{\parallel}$) for the pure and $BaTiO_3$ dispersed 6CHBT. The data above 3 MHz are influenced by the high frequency parasitic effect [21–22]. Inset shows the Cole- Cole plots. Hollow and solid symbols are respectively used for pure and dispersed systems.

(f_R) and distribution parameter (h). $\delta\varepsilon'_{\parallel}$ of pure sample is 6.8 and that of the dispersed sample is 6.0. Therefore, we find that dielectric strength of the dispersed sample is also decreasing by 12% as compared to that of the pure sample. The relaxation frequency of the pure 6CHBT is found to be 2.3 MHz (±30.9 kHz) and that of the dispersed 6CHBT is 2.4 MHz (±30.6 kHz) at 27.0°C.

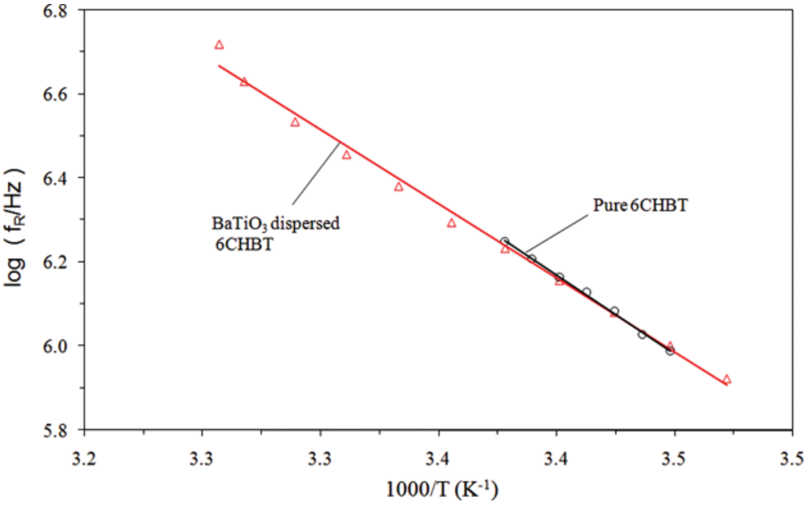

Figure 4. Arrhenius plots (log of the relaxation frequency with inverse of the temperature) for pure and $BaTiO_3$ dispersed 6CHBT. (Figure appears in color online.)

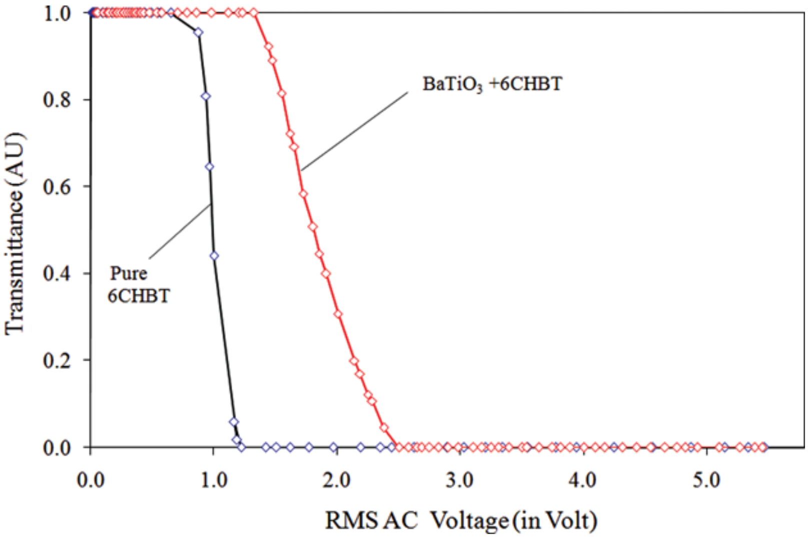

Figure 5. Transmission-voltage (T-V) curves for pure and $BaTiO_3$ dispersed 6CHBT. (Figure appears in color online.)

From the fitting, we observed that the relaxation frequency vary linearly with the reciprocal of the absolute temperature i.e it follows Arrhenius behavior ($f_R = Ae^{-Ea/kT}$). From the range of the frequencies and Arrhenius behavior, we conclude that this relaxation mechanism is due to the flip–flop motion of the molecules about their short axes. Activation energy (E_a) corresponding to the flip–flop motion of the molecules about their short axes is determined from the slopes of Figure 4 and it is 71 kJ/mole for pure and 68 kJ/mole for dispersed samples. The activation energy of the dispersed sample is found to decrease as compared to that of the pure. Ouskova *et al.* found that the activation energy in case of a nematic liquid crystal host doped with $Sn_2P_2S_6$ ferroelectric nanoparticles increases from 50 kJ/mole to 73 kJ/mole [14].

Figure 5 shows transmission intensity versus voltage curves for the pure and dispersed 6CHBT samples. Threshold voltage (V_{th} in volt) of the transmission–voltage curve (TVC) is determined from Figure 5. The threshold voltage of pure sample (6CHBT) increases after dispersion with $BaTiO_3$.

The various physical parameters obtained from the above studies are listed in Table 1.

4. Conclusions

From the above experimental results and discussion, we are able to conclude the followings:

- Due to the dispersion of $BaTiO_3$, isotropic to nematic transition temperature of 6CHBT decreases by about ~0.5°C and transition enthalpy is reduced by 24%.
- Longitudinal component of the dielectric permittivity of the $BaTiO_3$ dispersed 6CHBT decreases significantly and hence dielectric anisotropy also decreases by about 20%.

- The activation energy corresponding to the flip-flop motion of the molecules about the short axes of the $BaTiO_3$ dispersed 6CHBT sample is marginally reduced as compared to that of the pure sample.
- The threshold voltage of 6CHBT increases due to dispersion of $BaTiO_3$.

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