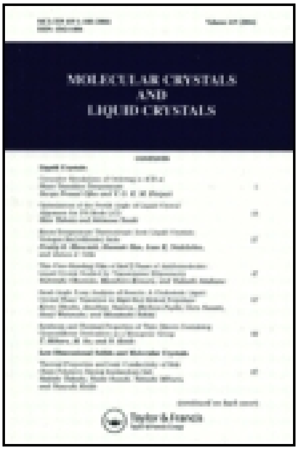

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In scope of this paper, dielectric and electro-optic properties of planar aligned ferroelectric liquid crystals/carbon nanotubes dispersions were investigated. It is demonstrated that even a small concentration of nanotubes greatly affects the performance of the liquid crystal cells. The obtained experimental results are explained by the trapping of ions through the carbon nanotubes, which results in a significant modification of the internal electric field as well as the space charges distribution inside the liquid crystal cells.

Keywords: carbon nanotubes; ferroelectric liquid crystals; rise time

INTRODUCTION

Liquid crystals are being extensively used in variety of applications such as displays, spatial light modulators (SLM), optical switches, holographic storage, etc [1–4]. In order to enhance the performance of these applications, it becomes necessary to synthesize new kind of liquid crystal materials. Standard techniques like chemical synthesis and preparation of new liquid crystalline mixtures lead to enhancement of some particular physical parameters. The similar task can

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also be performed by adding nanoparticles to the existing material. It has been demonstrated many times that addition of even very small quantity of nanoparticles can improve the physical properties of the existing liquid crystalline materials. Doping of nematic liquid crystals with various kinds of nanoparticles such as carbon nanotubes, $BaTiO_3$, MgO, Pd, $Sn_2P_2S_6$, SiO_2 have shown tremendous improvement in threshold voltage, switching time, and optical properties like increased photorefractivity [5–8]. In recent few years, ferroelectric liquid crystals (FLCs) have been the subject of intense research due to their potential applications in electro-optic devices. It becomes interesting to study doping of nanoparticles in FLCs in order to observe changes in their physical properties like spontaneous polarization, dielectric permittivity, tilt angle, switching time. A recent study has shown that adding gold (Au) nanoparticles in Felix 17/100 leads to lowering of threshold voltage and enhanced optical contrast [9]. Carbon nanotubes, due to their fascinating properties, are the most extensively studied material for making nanocomposites with liquid crystals [10–12]. In this paper, doping of carbon nanotubes in a multicomponent FLC mixture has been studied.

EXPERIMENTAL TECHNIQUE

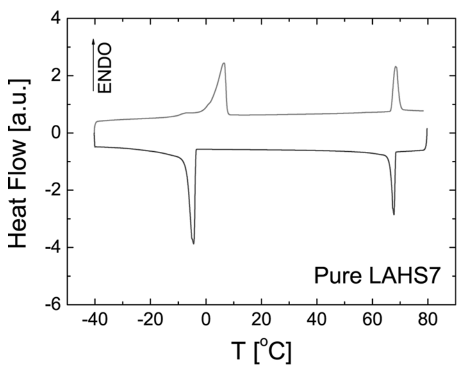
The ferroelectric liquid crystalline (FLC) material with acronym LAHS7 utilized in our experiments represented itself as a eutectic multicomponent mixture with a phenyl pyrimidine matrix. Multi walled carbon nanotubes (MWCNTs) were obtained from Plasma-Chem GmbH, Berlin. To prepare the FLC nanodispersions, MWCNTs were dispersed in tetrahydrofuran (THF) solvent and sonicated for 10 minutes using Bandelin Sonoplus ultrasonic mixer. The size of nanotubes was estimated by using Microtrack UPA particle size analyzer. The diameter of nanotubes used was ca. 30 nm, whereas the length was around 1 μm. The prepared dispersion was added to the pure LAHS7 in 0.01 wt% concentration. The residual solvent was removed by evaporation.

Texture observation was performed on pure and doped samples using a polarizing microscope with temperature controllable hot stage Mettler FP82. The textures of pure as well as doped samples were identical which confirmed that the nanotubes did not disturb the liquid crystalline molecular orientation. The electro-optical studies were performed on 5 μm thick ITO cells by using He – Ne lasers ($\lambda = 532.8$ nm, P = 1.5 mW), two crossed polarizers, temperature controlled chamber, a function generator (HP 33120A) and an oscilloscope (HP Infinium). The dielectric properties of the FLC/MWCNT nanodispersions were measured with the computer controlled impedance analyzer HP/Agilent 4192A. The temperature was maintained with a Eurotherm controller. The dielectric measurements were done in the wide temperature (up to the transition to the isotropic phase) and frequency range (10 Hz–10 MHz). The probing voltage was 100 mV.

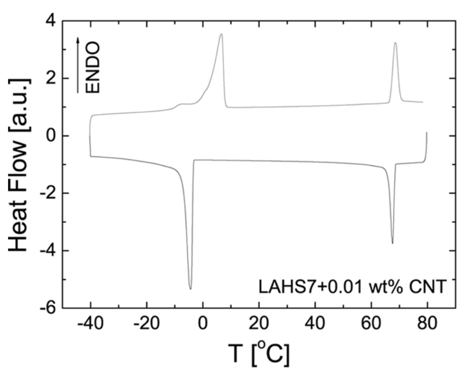
RESULTS AND DISCUSSION

DSC measurements have been done for pure as well as doped sample with cooling/heating rate 5 K/min (Figure 1).

The first peak on the heating curve is related to the melting point and the second one to the clearing point of the mixtures. It is worth



(a)



(b)

FIGURE 1 DSC curves obtained at heating/cooling rate of 5 K/min for (a) Pure LAHS7, (b) LAHS7 doped with 0.01 wt% MWCNTs.

noting that there is no significant change at the temperature of phase transitions between pure FLC mixture and the doped samples. However, the peaks are bigger for the doped sample (Fig. 1b) and this is due to the reason that mass of the doped sample taken for the DSC measurements was 3.95 mg and that of the pure sample was 3.73 mg. The phase sequence of the prepared mixture obtained from texture observation as well as DSC measurements is as follows:

$$\mathrm{Cr} \quad -4^{\circ}\mathrm{C} \quad \mathrm{SmC}^{*} \quad 56^{\circ}\mathrm{C} \quad \mathrm{SmA}^{*} \quad 68.5^{\circ}\mathrm{C} \quad \mathrm{I}$$

The measurements of the tilt angle (θ) did not demonstrate any significant influence of the nanotubes. In the room temperature the tilt angle was 22°. The spontaneous polarization versus temperature is presented in Figure 2. As one can see, for the pure LAHS7 as well as for the LAHS7 doped with 0.01 wt% MWCNTs the value is comparable.

Rise time was measured as the value between the 90% and 10% of the optical response of the sample to the applied square wave voltage signal. The value of electric field applied to the cells was 12 V/μm and the frequency was 10 Hz. The cells were carefully prepared and a homogeneous planar alignment was observed under polarizing microscope. Rise time versus temperature as presented in Figure 3 shows that the response of doped sample is faster than the pure one. One of the possible explanations for the improved electro-optical response can be the trapping of ions by MWCNTs and formation of electric double layers on the interface between FLC and alignment layers. In general, the depolarization field generated by ions on this interface is opposite to the electric field applied to the whole cell. In the case

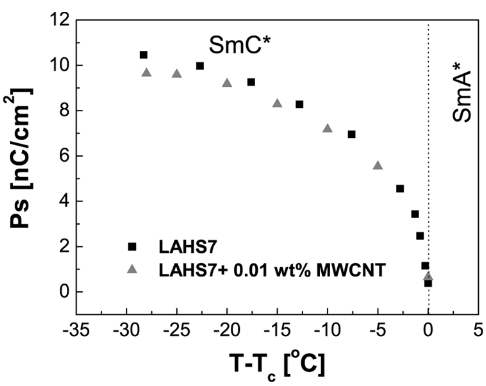


FIGURE 2 Spontaneous polarization vs. temperature for pure LAHS7 and LAHS7 doped with 0.01 wt% MWCNTs.

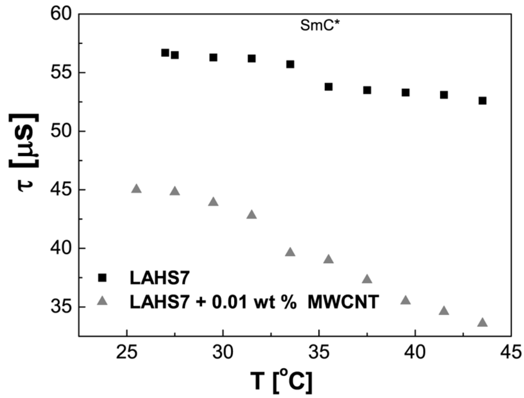


FIGURE 3 Temperature dependence of rise time.

of FLC/MWCNT nanodispersion, due to ion trapping the depolarization electric field should be lower compared to those of undoped FLC mixture. As a result, the response time is faster in case of nanodispersions.

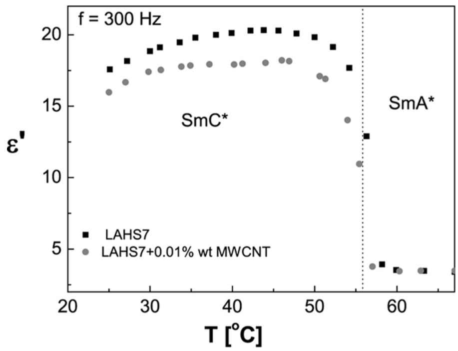
Figure 4 presents the real and imaginary part of the dielectric permittivity as a function of temperature. It can be seen that in the whole SmC* range, it is decreased with doping of MWCNTs.

In Figure 5, relaxation frequency of the Goldstone mode as a function of temperature is presented for the pure and the doped samples. It can be seen that the relaxation frequency shifts to the lower side for the doped sample. The relaxation frequency of the Goldstone mode (ν_G) is expressed as:

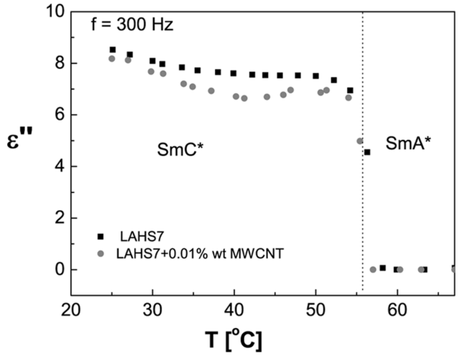
$$\nu_G = \Gamma K_3 q^2 / 2\pi$$

where, Γ is the inverse of the rotational viscosity, K_3 is the twist elastic constant and q is the wave vector of the pitch. With doping, the rotational viscosity increases and this leads to decrease in Γ and hence leads to shift of relaxation frequency to the lower side. Such a behavior was also observed for other FLC mixtures doped with dyes [13].

Dielectric absorption at different values of the bias field for pure and doped samples is presented in Figure 6. For the pure sample the value of 6 V is sufficient to suppress the Goldstone mode, whereas for the FLC mixture doped with 0.01 wt% MWCNTs much higher voltage (15 V) is needed. This interesting result confirms the fact that small amount of MWCNTs stabilized the helical structure of FLC.



(a)



(b)

FIGURE 4 Real (a) and imaginary (b) part of dielectric permittivity at 300 Hz for pure and doped samples.

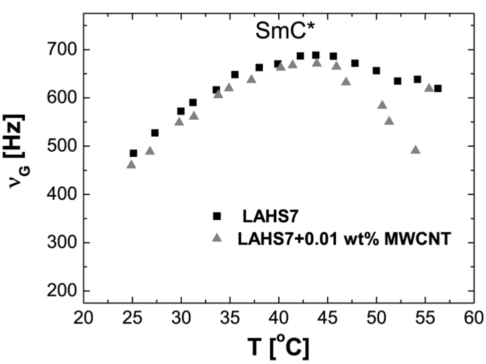
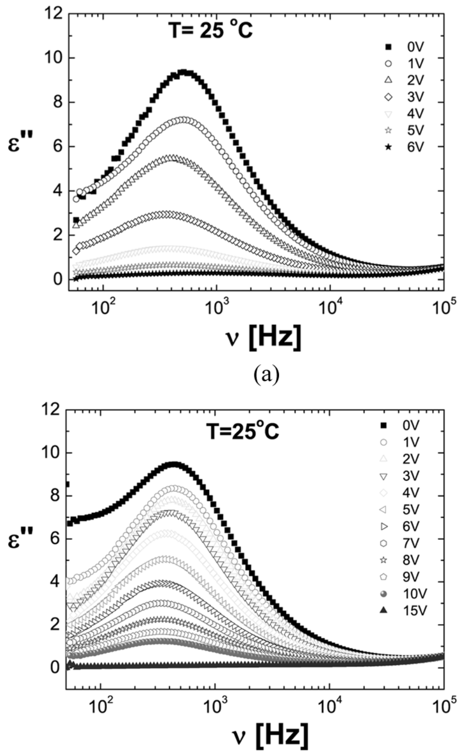


FIGURE 5 Temperature dependence of relaxation frequency of Goldstone mode for pure LAHS7 and LAHS7 doped with 0.01 wt% MWCNTs.



(a)
(b)

FIGURE 6 Dielectric absorption at different values of bias field for (a) Pure LAHS7 and (b) LAHS7 doped with 0.01 wt% MWCNTs.

As presented in Figure 4, both real and imaginary part of permittivity decreased for the doped sample. However, slight increase in the value of imaginary part of permittivity at lower frequencies for the doped sample was observed in bias measurements as shown in Figure 6. Bias measurements were performed after the temperature scan measurements and seem to show some temporal evolution of conductivity for the doped sample. Further measurements especially at low frequencies are required to support the above argument. These measurements are currently underway and will be presented elsewhere.

CONCLUSION

The influence of the multi walled carbon nanotubes on the dielectric and electrooptic properties of a ferroelectric liquid crystal mixture were studied. It was demonstrated that FLC/MWCNT dispersions had faster response time in comparison with undoped FLC. The most remarkable result is the decrease in the real and imaginary part of the dielectric permittivity of the FLC/CNTs with respect to that of the undoped sample. These effects can be explained by the high electron affinity of the nanotubes leading to the trapping of ions which results in a sufficient decrease of ion density in nanodispersions. One of the important observations is that only a small concentration of carbon nanotubes stabilizes the helical structure as more than double amount of voltage was needed to suppress the Goldstone mode for the doped sample.

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