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Temperature-dependent electrical and dielectric properties of nematic liquid crystals doped with ferroelectric particles

Yu-Cheng Hsiao [a], Sheng-Miao Huang [b], En-Rong Yeh [b], Wei Lee [a,*]

[a] Institute of Imaging and Biomedical Photonics, College of Photonics, National Chiao Tung University, Guiren Dist., Tainan 71150, Taiwan
[b] Department of Physics, Chung Yuan Christian University, Chungli 32023, Taiwan

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ABSTRACT

We report on the temperature dependence of dielectric properties of nematic liquid crystals impregnated with $BaTiO_3$ (BTO) ferroelectric nanoparticles. The behavior of ion transport at low frequencies is discussed by means of dielectric spectroscopy, which allows the ionic concentration and the relaxation time of electrode polarization to be deduced. The experimental results imply that the ferroelectric nanoparticles can not only increase the traveling time of ions between two electrodes but also suppress the buildup of the electric double layers. Verified by the voltage holding ratio of cells containing various contents of BTO nanoparticles, it is obvious that doping BTO into liquid crystals is a low-cost and easy way to improve the device performance.

1. Introduction

Dielectric particles embedded in nematic liquid crystal (LC) materials have recently been demonstrated to result in intriguing anisotropic colloids [1–7]. The colloidal particles in micrometer size generally form defects in LCs and ensembles of these particles and defects cause complex structures [8,9]. In comparison, colloidal particles in nanometer size, termed nanoparticles (NPs) thereafter, do not significantly perturb the nematic director field to produce considerable defects in LCs. However, to take advantage of the NP properties by combining the merits of both the NP material and the host, the concentration of NPs must be reasonably controlled in the limitation set by particle–particle aggregation arising from their large effective surface area. If the concentration of NPs as a dopant is high enough, even the weak deformations in the nematic director can create a rather viscous or an almost rigid suspension [4–6].

The effect of ferroelectric NPs (FNPs) dispersed in LCs has been of great scientific interest during the past few years [10–14]. For example, doping FNPs may give rise to an asymmetry in the electro-optical response of LCs [10], enhance the optical diffraction efficiency or beam coupling [11,12], alter the dielectric anisotropy, and shift the phase transition temperatures [13,14]. Beyond anisotropic media, Barner and coworkers found that the sensitivity of isotropic liquids to an applied electric field can be promoted by doping with FNPs [15]. They showed that a long milling process of ferroelectric barium titanate (BTO) particles with spontaneous polarization of 0.26 C/m^2 in the presence of surfactant can lead to a stable suspension in heptane. Clearly the nanoscale of the particles doped in a LC does not significantly disturb the overall LC orientation. As such, an optimal concentration of well-dispersed FNPs allows them to maintain their ferroelectricity and share their intrinsic properties with the LC matrix without inducing defects.

This study is concerned with the temperature-dependent dielectric dynamics properties of a specific nematic LC material doped with BTO FNPs. In recent year, it has been established that the unwanted impurity ions in LC displays strongly impact the device performance, reducing the display or image quality particularly at higher ambient temperatures [16,17]. In order to overcome the ion-induced problems such as decrease in voltage holding ratio (VHR) [18], increase in threshold voltage, image sticking, image flicking, and the slowdown of response speed, this work focuses on several essential ionic properties and tries to provide a promising solution to the field-screening nuisance and the ion-effect issue in general. Confirmed by the measurements of the VHR and dielectric spectroscopy, we demonstrate that doping BTO FNPs can effectively improve the performance of LC device in a reasonably wide working temperature range.

2. Experimental

We used the nematic LC E44 (Merck) and the BTO FNPs (Nanostructured & Amorphous Materials, Inc.) as the host and

* Corresponding author.
E-mail address: wlee@nctu.edu.tw (W. Lee).

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the nanodopant, respectively. E44, a eutectic mixture, has a high dielectric anisotropy $\Delta\varepsilon$ of 17.2 at 1 kHz and 25 °C as well as a high clearing point of ~100 °C [19]. BTO single crystals have a tetragonal crystal structure with the [001] polar axis and a spontaneous polarization of 26 μC/cm^2 at room temperature [20]. The dielectric constants of the BTO single crystals are 168 in the direction parallel to the polar axis and 2920 perpendicular to the polar axis [20]. The BTO particles employed in this work have an average size of 30–50 nm and possess an isotropic polyhedron particle shape. The LC suspensions were prepared by dispersing 0.05, 0.1, and 0.55 wt% of the said pristine BTO FNPs in E44. Each suspension was concocted by dispersing a mixture in an ultrasonic bath for 1 h and then by mechanical stirring for 30 min. The temperature of the ultrasonic bath was set at 95 °C (beyond the clearing point of E44). Finally, pure E44 and the colloids were injected by capillary action into planar-aligned test cells coated with indium-tin-oxide (ITO) layers. The cell gap is 11.3 ± 0.5 μm. The frequency-dependent complex dielectric constant $\varepsilon' - i\varepsilon''$ was acquired with an LCR meter (HIOKI 3522-50 LCR HiTESTER). The probe voltage amplitude is 500 mV$_{rms}$, smaller than the threshold voltage of the LC. On the other hand, the VHR is an important measure of LC display performance. It can be defined as [18]

$$\mathrm{VHR}(\%) = \frac{A_t}{A_i} \times 100\%, \tag{1}$$

where A_i and A_t represent the areas under the ideal and actual voltage curves during a frame time, respectively. The data line used in the VHR measurement of this study is a 5 V square-wave signal with a frame time of 16.67 ms, and the pulse width of the scan line is 15.6 μs at 60 Hz. A schematic of the VHR measurement is shown in Fig. 1. Totally, four types of samples having distinct FNP contents (0, 0.05, 0.1, and 0.55 wt%) were investigated in this work.

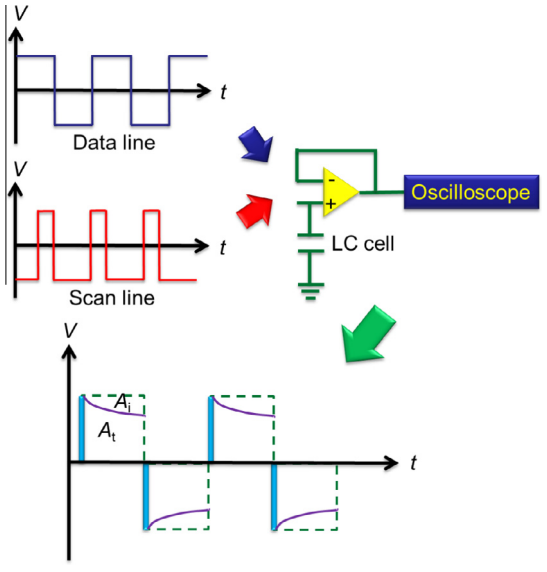

Fig. 1. Schematic of the VHR measurement and definitions of A_i and A_t used in the calculation of the VHR of a LC cell. The top panel shows the waveforms of the data-line as well as scan-line signals for charging a test cell. The bottom panel illustrates a typical output of the voltage-vs.-time plot. The charging time is determined by the pulse width of the scan line, lasting for 15.6 μs within a 16.67-ms frame. The VHR is calculated as the total area A_t under the charging time and the discharging curve for the remainder frame time divided by the ideal, rectangular area A_i across the total duration of the same frame. This value is usually obtained by averaging a number of ratios corresponding to a series of frames.

3. Experimental results and discussion

The frequency (f) range of the space-charge polarization induced by the ion effect is about between 1 and 10^2 Hz dictated by both the concentration and diffusion constant of impurity ions [21]. Furthermore, the characteristics of the electric double layer (EDL) can be explored by means of the dielectric data at frequencies lower than 1 Hz [22]. Figs. 2 and 3 present the real part $\varepsilon'(f)$ and the imaginary part $\varepsilon''(f)$ of the dielectric complex functions $(\varepsilon' - i\varepsilon'')$ of pure E44 and doped E44 at various temperatures, respectively. The temperature range for measurement is between 313 and 353 K, with an accuracy of about ±1 K. In the high-frequency range (10^4–10^5 Hz), $\varepsilon''(f)$ increased with increasing frequency for a given temperature. This observation is ascribed to the pseudo-relaxation originating from the cell geometries [23] rather than the molecular polarization of the NLC. Note that our empty cell can be regarded as a non-ideal capacitor whose effective capacitance and resistance are approximately 0.1 nF and 350 Ω, respectively, causing a cutoff frequency of *ca.* 5 MHz. The cutoff frequency shifts to a lower frequency of the order of 10^5 Hz due to the larger permittivity of the infiltrated NLC. Consequently, the dielectric complex curves at frequencies beyond 10^2 kHz do not relate to the NLC material's dielectric property. Figs. 2 and 3 also reveals an essential decrease in permittivity with increasing frequency in the frequency range of f < 10 Hz. This phenomenon is caused by relaxation of the near-electrode polarization due to a number of factors including EDLs, the space-charge polarization [24], and the near-electrode dipole polarization [25]. Thus, the frequency dependence of the NLC permittivity is very complex. In the low-frequency range (2–10^2 Hz) at room temperature, the frequency dependence of the dielectric complex is dominated by the electrode polarization [24], which can be elucidated by the behavior of impurity ions. It is worth mentioning that the errors in the dielectric data are very small and hence are neglected.

In accordance with Uemura's formulation [25,26], both $\varepsilon'(f)$ and $\varepsilon''(f)$ are given, respectively, by

$$\varepsilon'(f) = \frac{2nq^2D^{\frac{3}{2}}}{\varepsilon_0\sqrt{\pi}dk_BT} f^{-\frac{3}{2}} + \varepsilon_\infty, \tag{2}$$

and

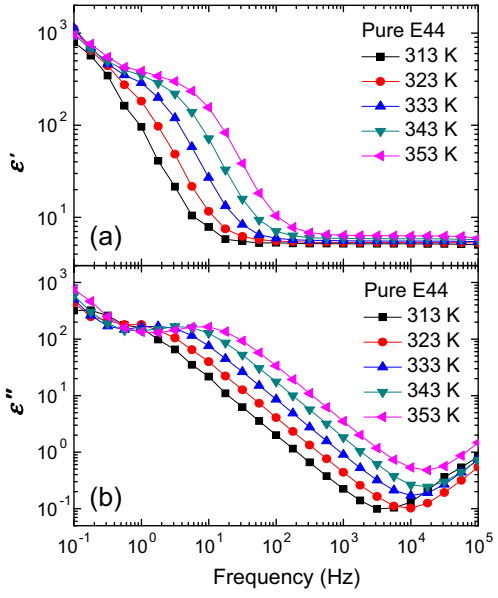

Fig. 2. (a) The real part and (b) imaginary part of the dielectric spectra of pure E44 at various temperatures.

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