Dielectric Studies in Spherical Silica Nanoparticles doped Ferroelectric Liquid Crystal Mixture

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Abstract. In this paper, spherical silica nanoparticles were doped into a ferroelectric liquid crystal (FLC) material. Dielectric studies were carried out in the frequency range of 20Hz-1MHz. Temperature and frequency dependent dielectric permittivity were investigated in the undoped and doped samples. It was observed that adding a small amount of SNPs, the permittivity increases ~20% than pure FLC mixture. A Goldstone mode was observed in both pristine FLC and SNPs doped FLC samples. The relaxation frequency of detected mode was also observed at ~570 Hz and ~715 Hz for pristine FLC and doped samples respectively at 34 °C. A single relaxation behaviour was also described in the form of Cole-Cole plot.

Keywords: Ferroelectric Liquid Crystals, Dielectric Spectroscopy, Permittivity, Goldstone Mode, Cole-Cole plot.

Introduction
After the discovery of a fascinated class of LC system i.e. ferroelectricity in liquid crystals by Meyer et al. (1975), various researchers have gained much interest in the electro-optical and memory devices based on FLCs owing to its fast switching response as compared to conventional liquid crystals [1]. During the last four decades, different research groups have worked for the improvement of various significant parameters of FLCs [2]. The improvement of electro-optical properties like switching time, spontaneous polarization and study the dielectric behaviour for flat panel displays, optical antennas, spatial light modulators etc. are the main concerns in FLCs [3-6]. Among dispersed LC systems, nanomaterials such as CdSe, CdTe, quantum dots, BaTiO3, Pd, Au, MgO, CNTs, etc. [7-9] doped liquid crystals composites have shown tremendous interest due to their unique electro-optic, thermal, mechanical and electrical properties. Nanoparticles doped ferroelectric liquid crystals have been studied owing to their interesting and prospective applications found specifically in technology.

Dielectric spectroscopy of FLC materials has been of keen interest and studied extensively both theoretically as well as experimentally. The dielectric studies of liquid crystalline materials provide information about the molecular arrangement, their dynamics and the intermolecular interaction. The value of dielectric permittivity depends upon many parameters like dipole moment, intermolecular interactions, rotational viscosity, conductivity and different motion of molecules under external field [10]. In the present work, dielectric properties of SNPs doped FLC is studied in SmC* phase and results have been compared with pristine ferroelectric liquid crystal material. The frequency and temperature dependence behaviour is also studied.
Experimental
In this study, FLC material trade name KCFLC10R procured from Kingston Chemicals, UK was used. Spherical silica nanoparticles (SNPs) of size ~ 80-85 nm and molecular weight 60.08 was obtained from M/S Sigma Aldrich, India. Liquid crystal cells having Mylar spacer of 5 µm thickness and an active area of 0.25 cm² obtained from Instec USA were used for investigations. SNPs-FLC suspension was prepared by dispersion of SNPs in 1 wt.% into FLC followed by ultrasonication at 36 kHz. The purpose of ultrasonication is to get homogenous mixture of SNPs-FLC. The prepared mixture was then injected into LC cells by capillary action above the clearing temperature of the liquid crystal material. The indium connections were made to filled cells for further study. The detail of cell preparation is given in our earlier work [7]. The sample cells were then inserted into hot stage (Linkam, UK) connected with programmable temperature controller (TP95, UK) and heated at a rate of 1°C/min. The temperature stability of hot stage was better than ± 0.1°C. The dielectric properties were investigated by Impedance Analyser (Wayne Kerr 6500B, UK) in the frequency interval 20Hz-10MHz. In order to measure the storage and loss modulus of permittivity, empty cells were calibrated with media having known permittivity. Here, we have used air and benzene for the calibration purpose.

Results and Discussion
Dielectric spectroscopy is a versatile tool for the investigation of molecular dynamics in liquid crystalline material. The complex dielectric permittivity, a function of both temperature and frequency is given by [11]

$$\varepsilon^*(\omega, \tau) = \varepsilon'(\omega, \tau) - j \varepsilon''(\omega, \tau)$$  (1)

where $\varepsilon'(\omega, \tau)$ and $\varepsilon''(\omega, \tau)$ are the real and imaginary values of complex dielectric permittivity used to calculate the storage and loss modulus respectively of the given material and $\omega = 2\pi f$ is the angular frequency of applied external field.

Frequency dependent dielectric permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) at constant temperature 34°C is shown in Figure 1(a & b). It is noticed that with the increase of frequency, the dielectric loss firstly increases and reaches a maximum value at about few hundreds Hz in the SmC* phase. Afterwards, loss diminishes and do not vary significantly. The frequency at which dielectric loss factor achieves its highest value is considered as relaxation frequency ($f_R$). This relaxation frequency is associated with Goldstone mode (arises due to phase fluctuations) occurs at low frequency region (~1kHz) [12]. Other types of relaxation modes such as new relaxation mode, soft mode and Domain mode have also been presented earlier [13,14] by various researchers but in this present study, only Goldstone mode was clearly seen at ~570 Hz and ~715 Hz for pristine and doped samples respectively.

![FIGURE 1](image-url)

**FIGURE 1.** Frequency dependence of (a) real part($\varepsilon'$) and (b) imaginary part($\varepsilon''$) of dielectric permittivity at 34°C for pristine FLC and SNPs doped FLC.
The relaxation behaviour expressed in the Cole-Cole plot is also presented in Figure 2. It is found that there is only one type of relaxation mode present in both pristine and SNPs doped FLC which is associated with Goldstone mode observed in the low frequency region (~1kHz).

FIGURE 2. Cole-Cole plot for pristine FLC and SNP doped FLC sample at 34°C.

Conclusions
In this work, SNPs in small quantity was dispersed in FLC mixture and studied its dielectric behavior in thin sample cell. An enhancement in dielectric permittivity in SNPs doped samples was observed than pristine FLC. A Goldstone mode of relaxation frequency (<1kHz) is found. The relaxation frequency slight shift towards higher frequency side after dispersion of SNPs in FLC.

Acknowledgements
The authors gratefully acknowledge the research project EMR/2016/003540 sponsored by SERB-DST, Government of India for the financial assistance. One of the authors (GK) is also thankful to Dr. Divya Jayoti, Research Associate, CeNS, Bengaluru for the experimental help.

References
[1] Meyer R B, Liebert L, Strzelecki L and Keller P 1975 J. Phys.(Paris)Let. 36 69-71
[2] Raina K K and Ahuja J K 1999 Mol. Cryst. Liq.Cryst. 338 125-140
[3] Srivastava A K, Misra A K, Chand P B, Manohar R and Shukla J P 2007 J. Phys. Chem.Solid 68 523
[4] Srivastava A K, Misra A K, Shukla J P and Manohar R 2008 Phys. Lett. A 372 6254
[5] Fratalocchi A, Asquini R and Assanto G 2005 Optics Express 13 32
[6] Neeraj and Raina K K 2010 Phase Transitions 83 615-626
[7] Chaudhary A, Malik P, Mehra R and Raina K K 2012 Phase Transitions 85 244
[8] Khushboo, Sharma P, Malik P and Raina K K 2018 Liquid Crystals 45(6) 896-906
[9] Singh D P, Visvanathan R, Duncan A E et al 2019 Liquid Crystals 46(3) 376-385
[10] S K Gupta Dielectric and Electro-Optical Study of Nanostructure Doped Liquid Crystal 2014
    PhD dissertation University of Lucknow
[11] Jayoti D, Malik P and Singh A 2015 AIP Conference Proceedings 1728 020647
[12] Gupta S K, Singh D P and Manohar R 2015 Adv.Mater.Lett. 6 68-72
[13] Chandel V S, Manohar S, Singh S P, Singh A K and Mahohar R 2013 Akademeia 3 1-5
[14] Kushwaha J K, Malik P, Raina K K and Arora V P 2011 Mol.Cryst. Liq. Cryst. 541 236-242