

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Low frequency dielectric relaxations of gold nanoparticles/ferroelectric liquid crystal composites

T. Joshi^a; A. Kumar^a; J. Prakash^b; A. M. Biradar^a

^a Liquid Crystal Group, National Physical Laboratory, New Delhi, India ^b Instrument Design Development Centre, Indian Institute of Technology Delhi, New Delhi, India

Online publication date: 15 November 2010

To cite this Article Joshi, T. , Kumar, A. , Prakash, J. and Biradar, A. M.(2010) 'Low frequency dielectric relaxations of gold nanoparticles/ferroelectric liquid crystal composites', *Liquid Crystals*, 37: 11, 1433 – 1438

To link to this Article: DOI: 10.1080/02678292.2010.520747

URL: <http://dx.doi.org/10.1080/02678292.2010.520747>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Low frequency dielectric relaxations of gold nanoparticles/ferroelectric liquid crystal composites

T. Joshi^a, A. Kumar^a, J. Prakash^b and A.M. Biradar^{a*}

^aLiquid Crystal Group, National Physical Laboratory, New Delhi-110012, India; ^bInstrument Design Development Centre, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India

(Received 18 May 2010; final version received 31 August 2010)

We present the characterisation and dielectric relaxation spectroscopy of a ferroelectric liquid crystal (FLC), namely KCFLC 7S. It was observed that the studied FLC material possesses the tendency of homeotropic alignment on glass substrates coated with indium tin oxide. A low frequency dielectric mode, along with the Goldstone mode, was observed in the SmC* phase of the FLC material. The low frequency mode became more dominant on doping gold nanoparticles into the FLC material. The occurrence of the low frequency mode was attributed to the ionisation–recombination-assisted diffusion of slow ions present in the FLC material. The behaviour of the relaxation frequency of the low frequency mode with applied dc bias and temperature was also demonstrated.

Keywords: ferroelectric liquid crystal; low frequency relaxation; gold nanoparticles

1. Introduction

Ferroelectric liquid crystals (FLCs) have attracted a great deal of attention from researchers due to their interesting features such as fast response and wide viewing angle characteristics [1–3]. Dielectric relaxation spectroscopy is a promising tool for investigating the molecular dynamics in FLCs. The study of the dielectric relaxation behaviour of liquid crystals (LCs) provides important information regarding its dipolar response to external stimulus.

Various dielectric modes have been found to exist in the smectic C* (SmC*) phase of FLC materials owing to either collective dielectric processes or the molecular reorientation processes connected with the polarisation of the molecules. The main collective processes involve Goldstone mode (GM), connected with the phase fluctuations in the azimuthal orientation of the director and soft mode due to fluctuations in the amplitude of the tilt angle [4–6].

Besides these dielectric processes, a number of other dielectric modes have also been observed in FLCs. In FLC materials having higher values of spontaneous polarisation (P_S), domain modes have been investigated [7]. The occurrence of these domain modes has been attributed to the formation of surface and bulk ferroelectric domains. Uehara *et al.* [8] observed a very low frequency mode (<1 Hz) and attributed it to the space charge accumulation on the interface of LC and polyimide layer. A thickness dependent low frequency mode (~50 Hz) has been detected in the SmC* phase of the FLC material H6/9 [9]. This mode has been attributed to the fluctuations of the director field modified by a non-homogeneous

ionic charge distribution across the sample. Havriliak *et al.* performed low frequency dielectric measurements in the SmC* phase of the FLC mixture named as Felix 18/100 and observed two separate peaks in the loss polarisability [10]. They examined the behaviour of these relaxation modes and found that the relaxation frequency has shifted towards low frequency side and high frequency side on increasing the bias field and temperature, respectively. Biradar *et al.* observed a Debye-like relaxation at very low frequency in non-chiral LCs. They found that the low frequency mode was taking place due to space charge accumulation in the surface alignment layer [11]. In a planar-aligned FLC cell, four relaxation processes namely Goldstone mode, domain mode, X mode and molecular mode have been observed in both the smectic X (SmX) and SmC* phases of the FLC [12].

Recently, dielectric relaxation studies of a surface-stabilised FLC with a chevron layer structure have been performed [13]. The authors have carried out the dynamic equation for collective molecular fluctuations under a weak alternating electric field and demonstrated that the chevron cells undergo two Debye relaxation processes connected with two chevron slabs on opposite sides of the interface plane. However, the low frequency dielectric relaxation process of FLCs seems to be affected by contributions of the ionic impurities present in the FLC materials. Pandey *et al.* studied the dielectric relaxation behaviour of a newly synthesised fluorinated anti-ferroelectric LC (namely 6F6B) and observed five different modes of dielectric relaxations in different phases of the material [14]. The authors observed a low frequency mode (mode 3)

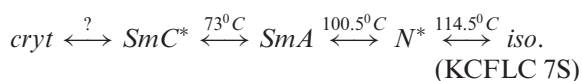
*Corresponding author. Email: abiradar@mail.nplindia.ernet.in

showing very strong dielectric strength in SmC^* phase and concluded that mode 3 had occurred due to the combination of the GM and ionic conductance mode.

In the present paper, we report the characterisation and low frequency dielectric relaxation of a FLC material, namely KCFLC 7S. The occurrence of a low frequency mode along with the GM in the SmC^* phase of the material is demonstrated. The effect of gold nanoparticles (GNPs) on the physical parameters and low frequency dielectric relaxation process of the FLC material is also discussed.

2. Experimental

The GNPs were synthesised using citrate reduction method [15] and characterised by high-resolution transmission electron microscope (HRTEM) (Technai G20-Stwin, USA). The typical size of the synthesised GNPs was around 20–30 nm. Highly conducting ($\sim 30 \Omega/\square$) indium tin oxide (ITO) coated glass plates were used to make sample cells. The desired electrode patterns on the ITO substrates were achieved using a photolithographic technique. The active electrode area was $0.45 \text{ cm} \times 0.45 \text{ cm}$. The thickness of the cell was maintained uniformly (from 1.2 to $11.0 \mu\text{m}$) using a photolithographic technique and Mylar spacers, respectively. The doping of GNPs in FLCs was pursued by adding $72 \mu\text{l}$ of a dispersion of GNPs in the FLC material used for a sample cell (2.4 mg). The homogeneous alignment was obtained on polymer coated glass plates using a buffing machine (LCBM, Irwin, USA). The vertical alignment was achieved due to intrinsic nature of the material (KCFLC 7S) used. The FLC or GNP-doped FLC materials were filled in isotropic phase by means of capillary action and then cooled gradually to room temperature. The phase sequence of the FLC mixture used is:



The dielectric studies of the FLC material were performed using an impedance analyser 6540 A (Wayne Kerr, UK) on the application of low ac measuring voltage of 0.5 V. The temperature of the sample cell was controlled by maintaining the temperature of water circulating through the sample holder using a Julabo temperature controller with an accuracy of 0.01°C . The temperature-dependent studies were carried out in a heating cycle. The determination of P_S and rotational viscosity (η) was performed using an automatic liquid crystal tester (ALCT, Instec, USA). For optical micrographs, the sample was mounted on a polarising microscope (Ax-40, Carl Zeiss, Germany) and the

transmission of normally incident polarised light through the sample was observed. The various phase transition temperatures of FLC material KCFLC 7S was determined by differential scanning calorimetry (DSC). The phase sequence of the KCFLC 7S is given above.

3. Results and discussion

Figure 1 shows the various material parameters at room temperature such as P_S , η , response time (τ_R) and tilt angle (θ) of the material KCFLC 7S with applied voltage as this FLC material is newly synthesised. The saturation value of P_S (Figure 1(a)) was observed around 14 nC/cm^2 , while the magnitude of η (Figure 1(b)) was observed as 125 mPa.s . The value of τ_R was observed to be of the order of milliseconds (Figure 1(c)). The saturation value of tilt angle (θ) (Figure 1(d)) was observed at around 25° . The different phase assignments and corresponding transition temperatures were determined at atmospheric pressure by DSC.

It was observed that the material KCFLC 7S favoured a homeotropic (HMT) alignment on ITO coated glass plates. Figure 2 shows the optical micrographs of KCFLC 7S material filled in different sample cells in which no surface treatment was made. One can clearly see a completely dark field of view of the sample cell under polarising optical microscope (Figure 2(a)), suggesting that the alignment is HMT. The tendency of this material to align homeotropically is found to be thickness dependent. The capability of HMT alignment was found to be dominant in thin cells ($\sim 2 \mu\text{m}$), whereas it reduced on increasing the cell thickness as can be seen from Figures 2(b) and 2(c).

It has been reported that the surfaces of the substrates such as glass, oxides and metals exhibit the ability to align LC molecules homeotropically [16], but the alignment in these cases showed a poor reproducibility and uniformity. Moreover, the material KCFLC 7S proved its importance in this concern showing a good uniformity and reproducibility of the HMT alignment for comparatively thin samples. The HMT alignment of the KCFLC 7S material was also confirmed by dielectric relaxation spectroscopy.

Figure 3 shows the behaviour of ϵ' of the homeotropically aligned sample cell filled with KCFLC 7S at different voltages at room temperature. It is clear from Figure 3(a) that the value of ϵ' is not suppressed even at higher values of applied voltages, suggesting the alignment to be HMT. In the case of the vertical alignment of the liquid crystals, the long molecular axis is perpendicular to the substrate's surface, preventing the occurrence of GM and leaving the only possibility of molecular rotation around their

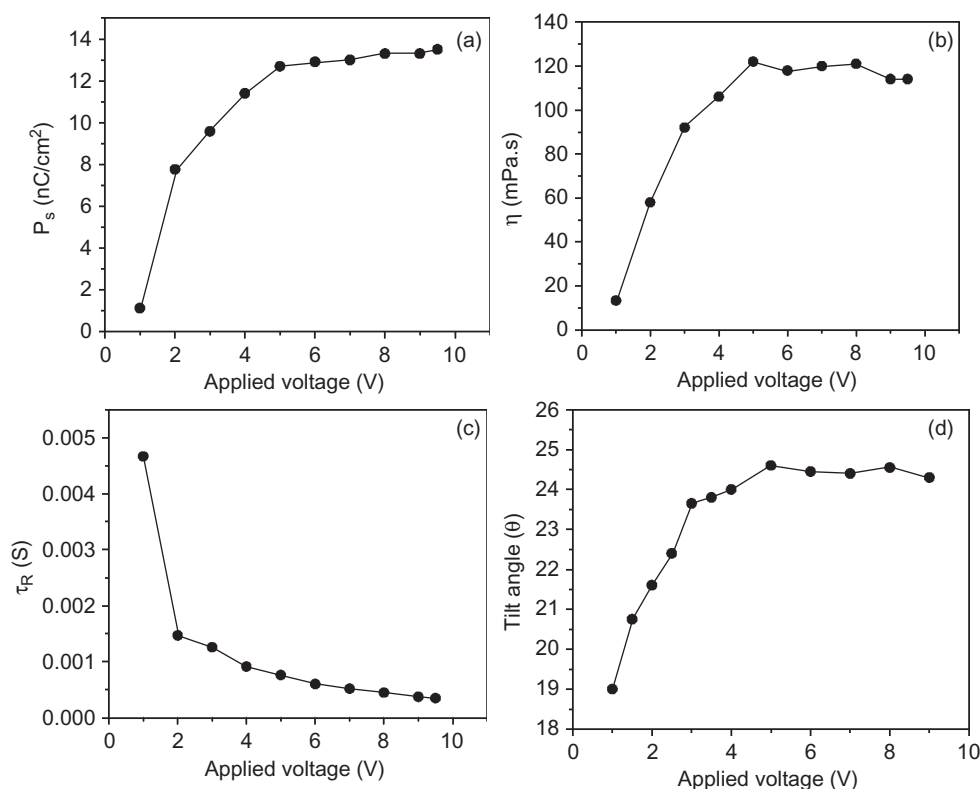


Figure 1. Behaviour of (a) spontaneous polarisation (P_s), (b) rotational viscosity (η), (c) response time (τ_R), and (d) optical tilt angle with applied voltage for FLC material KCFLC 7S at room temperature.

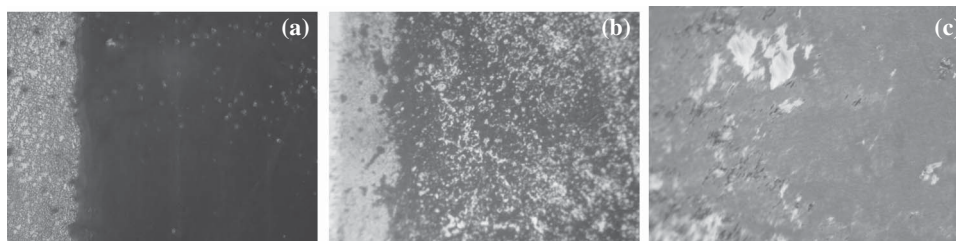


Figure 2. Polarising optical micrographs of FLC material KCFLC 7S filled in sample cells of thicknesses of (a) 1.2 μm , (b) 3.5 μm , and (c) 11 μm at room temperature (colour version online).

short molecular axis which gives the lower values of ε' . In addition, on the application of bias, the ε' value does not suppress remarkably for the homeotropically aligned LC cells. In perfect HMT alignment, the fluctuation of tilt angle does not occur and hence the occurrence of GM is ruled out. In fact, GM is not the characteristic feature of HMT alignment. It occurs only in homogeneously aligned geometries. The low value of permittivity is only due to molecular processes around the short axis of molecules. This lower value of permittivity can not be suppressed by a bias electric field because molecules are standing vertically on substrates. In vertical alignment, the stretching or rotation of the molecules is less along the short molecular

axis. The molecule does not experience the effect of bias.

Figure 3(b) shows the behaviour of $\tan \delta$ for the vertically aligned KCFLC 7S material, which shows a sharp relaxation peak at ~ 10 kHz frequency that corresponds to the molecular relaxations due to the motion of the molecule around its short axis. It is worth noting that the low frequency dielectric relaxation mode (~ 25 Hz) also took place in the case of a homeotropically aligned KCFLC 7S cell. This low frequency mode is not related to either dipolar relaxations (GM mode in planar cell configuration) or molecular processes around the short axis of molecules (molecular mode in vertical cell configuration). If it

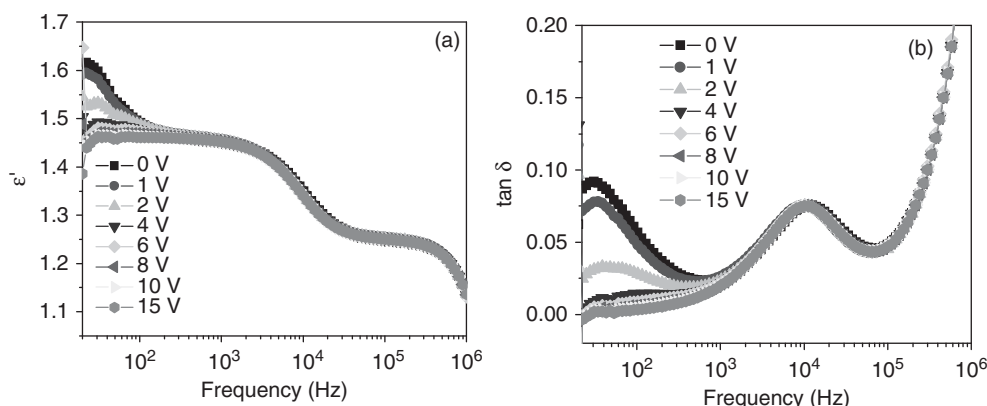


Figure 3. Behaviour of (a) dielectric permittivity (ϵ') and (b) dielectric loss factor ($\tan \delta$) as a function of log of frequency at different bias fields at room temperature of pure KCFLC 7S material cell of thickness $1.2 \mu\text{m}$ in vertical alignment configuration.

had been due to a molecular or any other collective dielectric relaxation process, then it would not have appeared in both (planar and vertical) alignment configurations. The existence of this mode is discussed in detail subsequently.

Figure 4 shows the behaviour of ϵ' and $\tan \delta$ of the FLC material KCFLC 7S with frequency at room temperature in a planar aligned cell. A weak signature in the form of a dip in ϵ' was observed, suggesting the occurrence of a low frequency (~ 100 Hz) relaxation mode along with the GM (Figure 4(a)). Figure 4(b) shows the two relaxation peaks in which the peak at the high frequency side corresponds to the GM, whereas the low frequency peak is related to the low frequency relaxation of the material. This low frequency mode can not be assigned either as GM or the mode purely due to space charge accumulation near the substrate surface. The occurrence of this mode is related to the relaxations of the ionic impurities present in the material and is discussed later.

The doping of nanostructured materials into LCs has emerged as a fascinating area of research from the application point of view. The addition of nanoparticles (NPs) has improved many of the special characteristics of FLCs in the form of non-volatile memory effect, faster electro-optic response, low driving voltage, enhanced photoluminescence, and NPs induced vertical alignment [17–21]. On the basis of earlier studies, we doped GNPs into the KCFLC 7S material and examined their effect on electro-optical and dielectric relaxation properties. It was observed that the value of the threshold voltage is reduced remarkably on the doping of GNPs into the KCFLC 7S material. However, the value of saturation of P_S and η was not affected much.

Figure 5 shows the behaviour of $\tan \delta$ of pure and GNP-doped KCFLC 7S material with frequency at different temperatures. Figure 5(a) shows the occurrence of a low frequency relaxation peak along with

the GM. It was observed that the relaxation frequency (ν_R) of the low frequency mode as well as GM shifted towards the high frequency side on increasing the temperature. It is very interesting to see that the low frequency relaxation peak was resolved clearly on the doping of GNPs in the KCFLC 7S material (Figure 5(b)). The amplitude and ν_R of the low frequency mode was found to increase with increasing temperature. It was also observed that the amplitude of the low frequency peak nearly equalled the amplitude of GM at a temperature very near to the $\text{SmC}^*-\text{SmA}^*$ phase transition (T_C) and it dominated over GM mode in the vicinity of T_C of the material.

On the basis of these observations, it is clear that the low frequency relaxation process was resolved by doping of GNPs into KCFLC 7S. Thus, the occurrence of the low frequency peak is related with the ionic impurities present in the material. Figure 6 shows the variation of the resistance with frequency at different temperatures for pure and GNP-doped KCFLC 7S material. From Figure 6, it can be seen that the resistance (or ionic conductivity) has been reduced (or enhanced) on the doping of GNPs into the material. The reason behind the occurrence of this low frequency relaxation mode lies in the relaxations of the ionic charges through single particle diffusion of fast ions and ionisation–recombination-assisted diffusion of slow ions.

Jin and Kim studied the low frequency dielectric relaxations of a non-chiral (8CB) LC material [22]. They performed a numerical simulation and concluded that the ionic impurities contribute to low frequency dielectric relaxations in two separate ways – from fast ions in the single particle diffusion and slow ions in the ionisation–recombination assisted diffusion. They defined a characteristic time (τ_K) for the ionisation–recombination process and expected to observe one single peak shifting to the low frequency side with increasing field strength, due to the

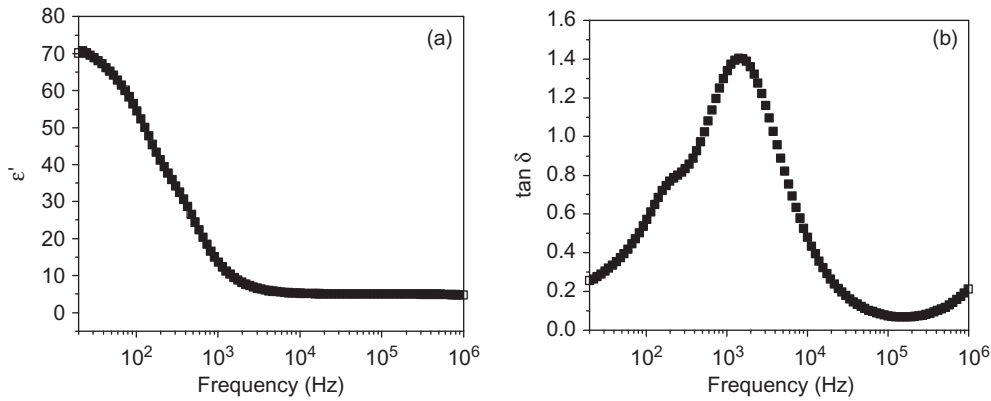


Figure 4. Behaviour of (a) dielectric permittivity (ϵ') and (b) dielectric loss factor ($\tan \delta$) as a function of log of frequency at room temperature of pure KCFLC 7S material cell of thickness $4 \mu\text{m}$ in planar alignment configuration.

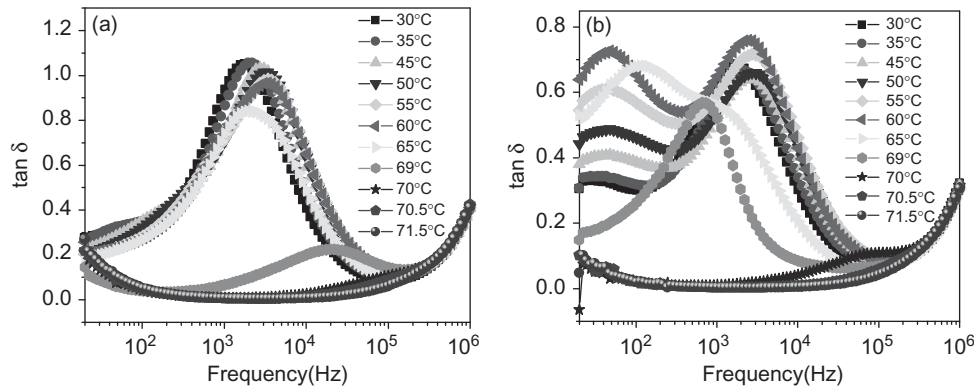


Figure 5. Behaviour of dielectric loss factor ($\tan \delta$) as a function of log of frequency at different temperatures of (a) pure KCFLC 7S material (b) GNP-doped KCFLC 7S material cells of thickness $4 \mu\text{m}$ in planar alignment configuration.

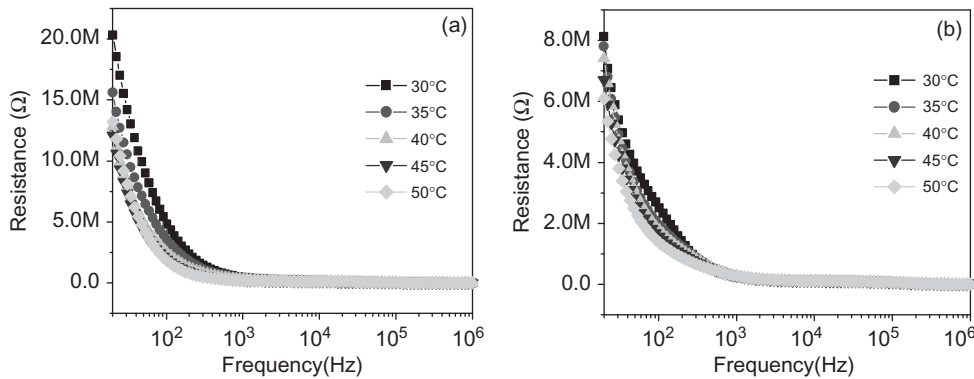


Figure 6. Variation of resistance as a function of log of frequency at different temperatures of (a) pure KCFLC 7S material (b) GNP-doped KCFLC 7S material cells of thickness $4 \mu\text{m}$ in planar alignment configuration.

ionisation–recombination effect, in the low frequency regime under the condition $\omega_p < \omega_n < \tau_K^{-1}$, where ω_p and ω_n are the peak frequency of the slow and fast ions, respectively [22].

In our case, one other relaxation peak corresponding to the GM along with the low frequency peak was observed as we used a chiral LC system having the SmC^* phase. The low frequency mode in

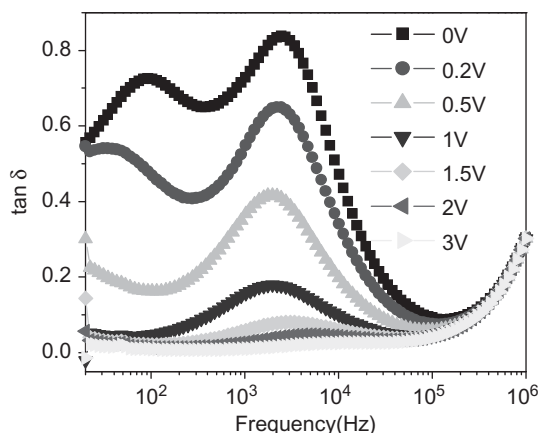


Figure 7. Behaviour of dielectric loss factor ($\tan \delta$) as a function of log of frequency at different bias fields at 55°C of GNP-doped KCFLC 7S material cell of thickness 4 μm in planar alignment configuration.

KCFLC 7S material appeared due to the ionisation–recombination assisted diffusion of slow ions in planar alignment configuration, which was resolved clearly by doping of GNPs (Figure 5). This mode also appeared in the case of vertically aligned (without using alignment layer) cells of KCFLC 7S material (Figure 3). The low frequency mode in vertically aligned cells appeared due to single particle diffusion of fast ions and the peak frequency is found to be almost independent of applied bias field [22]. The effect of bias field on the low frequency peak of GNP-doped KCFLC 7S material was observed as shown in Figure 7. It is clear that the ν_R of the low frequency mode shifted towards the low frequency side on increasing the bias field across the sample.

4. Conclusions

We have characterised a newly synthesised FLC mixture (KCFLC 7S) and studied the low frequency dielectric relaxation of this material. It was found that the material KCFLC 7S possesses the capability of homeotropic alignment on ITO coated glass substrates without any surface treatment. A low frequency relaxation mode, along with the GM, was detected in the SmC^* phase of the material KCFLC 7S as well as in other FLC mixtures. The low frequency mode was found to be dominant in GNP-doped FLCs due to the increased ionic conductivity. The relaxation frequency of this low frequency mode was shifted towards the low frequency side by the application of bias field across the cell. The occurrence of this low frequency peak was attributed to the effective ionisation–recombination effect in the low frequency regime due to presence of ionic impurities in the FLC materials.

Acknowledgements

The authors sincerely thank Professor R.C. Budhani, Director of the National Physical Laboratory, for continuous encouragement and interest in this work. We also sincerely thank Dr P. Goel, Dr I. Coondoo, Mr A. Choudhary and Ms A. Malik for fruitful discussions. The authors (T.J. and A.K.) and J.P. wish to thank the University Grant Commission (UGC) and the Council of Scientific and Industrial Research (CSIR) for providing financial assistance.

References

- [1] Meyer, R.B.; Lieber, L.; Strzelecki, L.; Keller, P. *J. Phys. Lett. (Paris)* **1975**, *36*, 69–71.
- [2] Clark, N.A.; Lagerwall, S.T. *Appl. Phys. Lett.* **1980**, *36*, 899, (1–3).
- [3] Dijon, J. In *Liquid Crystals: Applications and Uses*: Bahadur, B., Ed.; World Scientific: Singapore, 1992; Vol. 1, pp 305–360.
- [4] Levstik, A.; Carlsson, T.; Filipic, C.; Levstik, I.; Zeks, B. *Phys. Rev. A: At., Mol., Opt. Phys.* **1987**, *35*, 3527–3534.
- [5] Hiller, S.; Beresnev, L.A.; Pikin, S.A.; Haase, W. *Ferroelectrics* **1996**, *180*, 153–163.
- [6] Kundu, S.K.; Suzuki, K.; Chaudhuri, B.K. *J. Appl. Phys.* **2003**, *94*, 2271–2276.
- [7] Beresnev, L.A.; Pfeiffer, M.; Pikin, S.A.; Haase, W.; Blinov, L. *Ferroelectrics* **1992**, *132*, 99–114.
- [8] Uehara, H.; Hanakai, Y.; Hatano, J.; Saito, S.; Murashiro, K. *Japan. J. Appl. Phys.* **1995**, *34*, 5424–5428.
- [9] Novotna, V.; Glogarova, M.; Bubnov, A.M.; Sverenyak, H. *Liq. Cryst.* **1997**, *23*, 511–518.
- [10] Havriliak, S., Jr.; Vij, J.K.; Ni Ming. *Liq. Cryst.* **1999**, *26*, 465–467.
- [11] Biradar, A.M.; Kilian, D.; Wrobel, S.; Haase, W. *Liq. Cryst.* **2000**, *27*, 225–231.
- [12] Kundu, S.K.; Yagihara, S. *Jpn. J. Appl. Phys.* **2007**, *46*, 3211–3213.
- [13] Jezewski, W.; Kuczynski, W.; Hoffmann, J. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2006**, *73*, 061702 (1–10).
- [14] Pandey, G.; Dhar, R.; Agrawal, V.K.; Dabrowski, R. *Physica B* **2007**, *393*, 167–174.
- [15] Turkevich, J.; Stevenson, P.C.; Hillier, J. *Discuss. Faraday Soc.* **1951**, *11*, 55–75.
- [16] Cognard, J. *Mol. Cryst. Liq. Cryst. Suppl. Ser.* **1982**, *1*, 1–74.
- [17] Prakash, J.; Chaudhary, A.; Kumar, A.; Mehta, D.S.; Biradar, A.M. *Appl. Phys. Lett.* **2008**, *93*, 112904 (1–3).
- [18] Prakash, J.; Chaudhary, A.; Mehta, D.S.; Biradar, A.M. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2009**, *80*, 012701 (1–4).
- [19] Lee, W.; Wang, C.-Y.; Shih, Y.-C. *Appl. Phys. Lett.* **2004**, *85*, 513 (1–3).
- [20] Kumar, A.; Prakash, J.; Mehta, D.S.; Biradar, A.M.; Haase, W. *Appl. Phys. Lett.* **2009**, *95*, 023117 (1–3).
- [21] Kumar, A.; Prakash, J.; Goel, P.; Khan, T.; Dhawan, S.K.; Silotia, P.; Biradar, A.M. *Eur. Phys. Lett.* **2009**, *88*, 26003 (1–6).
- [22] Jin, M.Y.; Kim, J.-J. *J. Phys. Condens. Matter* **2001**, *13*, 4435–4446.