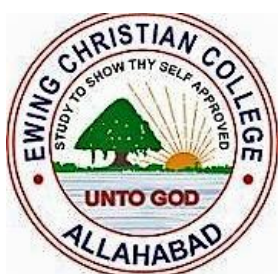


Project
on
Dielectric properties of Ferroelectric Liquid Crystals : A Review



Submitted by

Kameshwar Dubey

Master of Science

in

Department of Physics

Ewing Christian College, Prayagraj

Session 2019-21

Supervisor

Dr. S. K. Chirra

Department of Physics

Ewing Christian College

Co-Supervisor

Dr. (Mrs.) K.L.Pandey

Department of Physics

Ewing Christian College

Acknowledgement

The success and final outcome of this project required a lot of guidance and assistance from many people and I am extremely fortunate to have got this all along the completion of my project work. Whatever I have done is only due to such guidance and assistance I would not forget to thank them.

I respect and thank ***Dr. Saikumar Chirra sir*** for giving me an opportunity to do this project work and providing us all support and guidance which made me complete this project on time. I would like to express my gratitude towards ***Dr. (Mrs.) K. L. Pandey*** mam, for providing me practical laboratory and all other support for project.

I would also like to thank our H.O.D. ***Dr. A. K. Singh*** sir for giving me such a wonderful opportunity.

Last but not least I would like to thank my parents who helped me financially and encouraged me throughout the completion of the project.

CERTIFICATE

This is to certify that the work , “**Dielectric properties of Ferroelectric Liquid Crystals : A Review. ”** is a bonafide work done and submitted by **Kameshwar Dubey (ECC1864009)** in the partial fulfilment of the award of **M.Sc. degree in Physics** during the academic year **2019-21** of **Ewing Christian College** , Prayagraj (An autonomous constituent college of **University of Allahabad**).

Dr. Anil Kumar Singh (H.O.D.)

Department of Physics

Abstract:

In the present work I am reporting the dielectric behavior of three FLC series namely **QMn/m**, **En/m** and **QVE n/m**.

The complex permittivity has been utilized to determine the Dielectric strength($\Delta\epsilon$), relaxation time (τ_r), and relaxation frequency (f_r) and the temperature dependence of relaxation time and relaxation frequency for all the investigated chiral FLC. The tilted ferroelectric SmC* phase of three structurally different series having three aromatic rings in the core structure connected by ester groups with different end alkyl chain lengths, all of which are derived from lactic acid, have been observed by broadband dielectric spectroscopy. The dielectric spectra strongly depend both on the temperature as well as the specific molecular structure of the self-assembling compounds possessing the ferroelectric polar order. The results reveal a strong Goldstone mode in the ferroelectric SmC* phase with \sim kHz relaxation frequency. In the SmC* phase, the real and imaginary parts of the complex permittivity increase up to certain temperature near the SmC*-N*/SmA* transition and then decrease with increasing temperature, perhaps due to the disruption of the molecular domains at the onset of the SmA*/N* phase transition. The dielectric strength attains a maximum value in the SmC* phase and then decreases near the SmA*/N* phase transition. The dielectric strength is also influenced by the length of the alkyl chain and the nature of connecting unit of constituent molecules.

1. INTRODUCTION :

1.1 LIQUID CRYSTALS –

Most substances exist in three phases: solid (often crystalline), liquid and vapour. The difference between these states of matter is the degree of order in the material, which is directly related to the surrounding temperature and pressure. At low temperatures, when the material is in its solid state, the constituents (atoms, ions or molecules) cannot move about freely. Their only movements are thermal vibrations about an equilibrium position (see the left image below).

If the temperature is raised, more energy is put into the system, leading to stronger and stronger vibrations. Finally, at the transition temperature between the solid and liquid states, the long range positional order is broken and the constituents may move about in a random fashion (center image), constantly bumping into one another and abruptly changing direction of motion. The thermal energy is still not, however, high enough to completely overcome the attractive forces between the constituents, so there is still some positional order at short range. Because of the remaining cohesion, the density of the liquid is constant even though, as opposed to the solid, the liquid takes the shape of its container. If we keep on raising the temperature until the next phase change, the substance enters its gas (or vapour) state and its constituents are no longer bound to each other.

The molecules in a liquid crystal phase diffuse about much like molecule of a Liquid, but as they do so they maintain some degree of orientational order and some time some positional order also. The amount of order in a liquid crystal is quite small relative to a crystal. There is only slight tendency for the molecule to point more in one direction than others or to spend more time in various positions than other. The fact that most of the order of a crystal is lost when it transform to a liquid.

- It is the intermediate or the interdisciplinary state between the solid and liquid where as the molecule are free to move but are oriented in a particular manner. The molecules have no positional order but retain some orientational order.
- Liquid crystal phase is also called meso phase and the molecules, which can exist in mesophase, are called Mesogens.

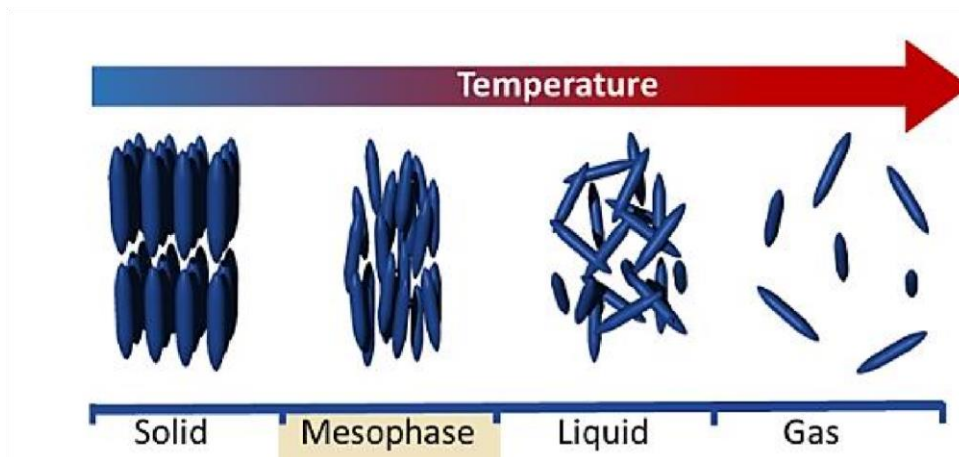


Figure.1 Allignment of molecules with variation of Temperature

Image citation:<https://www.slideshare.net/knowledge1995/liquid-crystals-57084227>

Liquid crystals are most widely used in display devices. By the end of the 20th century, the market size of liquid crystal displays LCDs alone grew above \$20B and is now replacing conventional cathode-ray tubes CRTs with better options. Twisted nematic TN liquid-crystal display[1] was reported in 1971 and it found application in watches and calculators as low-information-content LCDs. TN displays are not suitable for high-information-content displays as their contrast ratio is low and the viewing angle narrows when driven at a high multiplexing ratio. Around 1985 a prototype supertwisted nematic STN display was demonstrated[2-3] STN displays have a steep electro-optical response, and can be used for high-information displays. However, the STN viewing angle is worse than the TN viewing angle and contrast is no better. The only reason for using STN is its higher multiplexability in passive matrices. Active thin-film transistors TFTs employ TN. STN displays are now used in mobile telephones, personal digital assistants PDAs, and word processors. However, the response speed of STN LCDs is low, and unsuitable for video applications. They have several disadvantages in resolution, multiplexing level, response time, color, and viewing angle as well. In 1975, Meyer et al. reported ferroelectricity in the chiral SmC SmC* phase of liquid crystals. [4-5] With the discovery of ferroelectric liquid-crystals FLCs, it seemed that the search of the appropriate material for video application is over when technical application of FLCs was suggested by Clark and Lagerwall[6]. Ferroelectric LCDs seem to be the most promising LCD due to their extremely fast switching speed and capability for high level of multiplexing. The problems of STN LCDs have been removed in ferroelectric LCDs FLCs to a large extent with improved switching time 0.1 ms and bistability, but not completely. There are several problems in the commercialization of FLCs. Some of them are the small cell spacing 1–2 micrometer, the problem of the mechanical shock due to unstable molecular anchoring at the surface, and above all the desired gray scale can only be achieved by indirect methods such as spatial or temporal dithering. Recently antiferroelectric liquid-crystal materials have been proposed as prospective material for use in display devices AFLCDs. [7-13] The antiferroelectric liquid crystals AFLCs are attractive for their tristate switching behavior, easy dc compensation, microsecond response, hemispherical viewing angle in-plane switching geometry, intrinsic analog gray-scale capability, and no-ghost effect. AFLCDs are still in the stage of development and further studies are needed for mass-scale applications. Studies of antiferroelectric liquid crystals are important not only from the application point of view but also from the point of view of basic studies as AFLC materials are showing submesophases such as SmC_α*, SmC_β* with the existence of second order transitions.

1.2 CLASSIFICATION OF LIQUID CRYSTALS :

Liquid crystals can be broadly classified into two categories

- **Thermotropic liquid crystal:** Those liquid crystal which exhibit liquid crystalline state on change of temperature alone. This type of liquid crystal depends on the temperature and the thermotropic behavior of the sample. Example–para-Azoxyanisole etc.
- **Lyotropic liquid crystal :** These exhibit liquid crystalline state in mixture and when the concentration of one of the constituents is varied .Example–Soap.

A number of different types of molecules form liquid crystal phases what they all have in common is that they are anisotropic . Either their shape is such that one molecular axis is very different from the other two or in some cases, the interaction between these anisotropic molecules promote orientational and some time positional order in another fluid phase.

The two most common type of molecule that form liquid crystals phases is a rod shaped molecule such compound are called **Calamatic** liquid crystal and many different phases are possible likewise those crystals which have the disc like shape are called the **Discotic** liquid crystal.

Thus, liquid crystals can be classified as follows

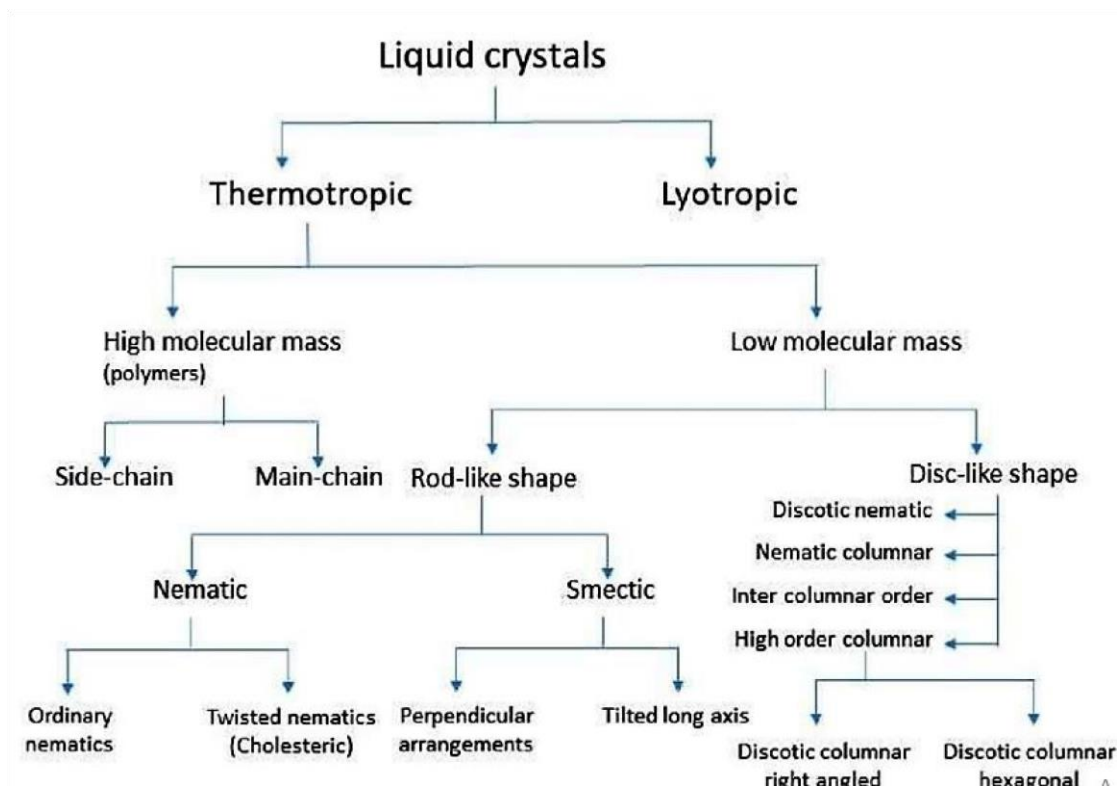


Figure 2 Classification of Liquid Crystals

1.3 NEMATIC LIQUID CRYSTALS :

A nematic liquid crystal is a transparent or translucent liquid that causes the polarization (that is, the focusing in a plane) of light waves to change as the waves pass through the liquid. The extent of the change in polarization depends on the intensity of an applied electric field. Nematic comes from a Greek prefix *nemato* meaning threadlike and is used here because the molecules in the liquid align themselves into a threadlike shape. Nematic liquid crystals are used in twisted nematic displays, the most common form of liquid crystal display.

A typical nematic liquid crystal produces a 90-degree shift in the polarization of the light passing through when there is no electric field present. When a voltage is applied, an electric field is produced in the liquid, affecting the orientation of the molecules. This causes the polarization shift to be reduced. The effect is slight at low voltages, and increases as the voltage (and the resulting field strength) increases. When the applied voltage reaches a certain level, the polarization shift disappears entirely.

Because their light transmission properties can be deliberately varied as a function of applied external voltage, nematic liquids are used in alphanumeric liquid-crystal displays (LCDs), such as those found in digital wristwatches and many consumer electronic devices

1.3.1 Properties of Nematic Liquid Crystals.

- They have thread like structure.
- Formed from optically inactive compounds.
- Do not have any positional order but the molecules are arranged parallel to one another means they have orientational order.
- Less viscous as they are closely arranged .and fluidity is more .

Example: Cyanobiphenyls

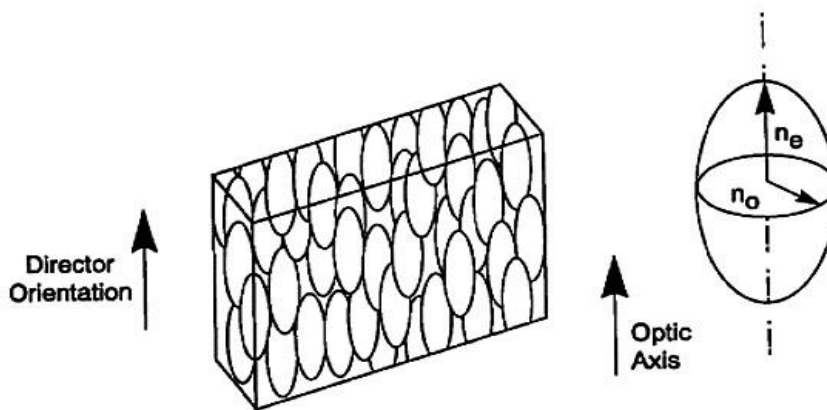


Figure 3 Nematic liquid crystal.

Image Citation : http://barrett-group.mcgill.ca/tutorials/liquid_crystal/LC02.htm

1.4 SMECTIC LIQUID CRYSTALS :

There is a two-dimensional layered structure caused by more positional limitations compared with that of a nematic phase. A smectic phase is harder than a nematic phase, because the movable range of the unit molecules is relatively narrow. A nematic phase sometimes changes to a smectic phase by decreasing the temperature. Diversity of the layered structures demonstrates many kinds of smectic phases. The name Smectic comes from the Greek word for soap, since the mechanical properties of these phases reminded early phases of soap system. The important feature of a smectic mesophase, which distinguishes it from a nematic or a cholesteric one, is its stratification. The molecules are arranged in layers and exhibit some correlation in their position in addition to the orientation ordering. The layer can slide easily over one another. Depending on the molecular order in layers, a number of different types of smectic have been observed. Such that the most common are Smectic A and Smectic C.

In a Smectic A, molecules are aligned perpendicular to the layers, without long range crystalline ordering within them. In Smectic C, the preferred molecular axis is not perpendicular to the layers, so that the phases have biaxial symmetry. In Smectic B, there is hexagonal crystalline order within the layers.

A number of compounds have both nematic and smectic mesophase. As a general rule, the lower phases have a greater degree of crystalline order. The nematic mesophase always occurs at a higher temperature than the smectic one; smectic mesophase occurs in the following order; A–C–B as the temperature decreases.

The smectic phase of liquid crystal, which is defined as being equivalent to the slippery, thick residue found at the bottom of soap dishes, is characterized by a slight degree of translational order in the crystal molecules which is not found in the nematic phases. While keeping similar orientation and pointing in the same direction as the molecules in nematic liquid crystals do, in this phase the molecules tend to line themselves up into layers. While these layers as a whole move freely, movement within the layers is restricted; therefore, it creates a slightly more solid substance. Smectic liquid crystals have been found to have fast electro optical response time and because of this it is used along with nematic liquid crystals, in producing LCD screens.

1.4.1 Properties of Smectic Liquid Crystals.

- Molecules are arranged in layer. At any instant of the time the number of molecules within a layer is much more than the number of molecules between the layers. □ Highly viscous as they are closely arranged.
- Fluidity is less.
- Depending on the orientation of the molecules smectic liquid crystals are further classified into different types like smectic A, B, C.

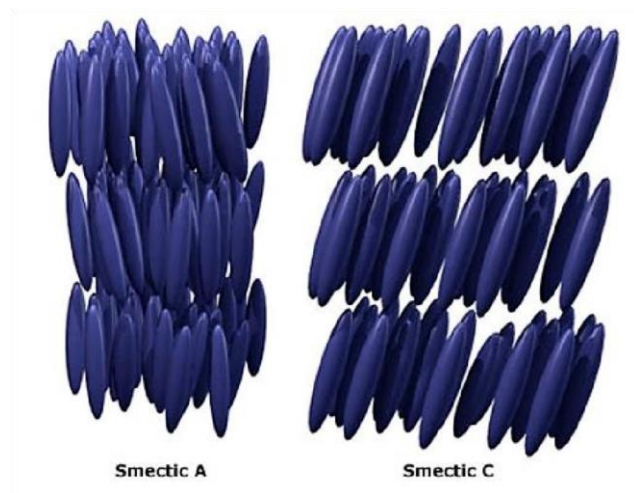


Figure 4 Different type of Smectic liquid crystals are shown above

Image citation : https://www.researchgate.net/figure/LC-molecular-arrangement-in-a-smectic-A-phase-and-b-a-smectic-C-phase-where-n-is_fig3_281127525

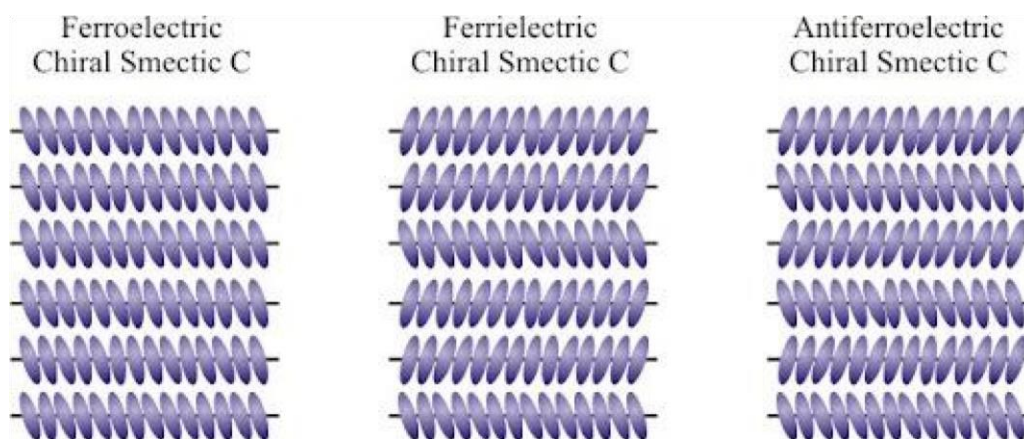


Figure 5 Different types of Chiral Smectic C liquid crystals

Image citation : <http://www-g.eng.cam.ac.uk/CMMPE/OldSite/lcintro2.html>

1.5 CHOLESTERIC LIQUID CRYSTAL :-

Cholesteric is the nematic state superimposed with a natural twist between layers including the long axis of molecule induced by incorporation of chiral group to give helical twist to the orientation of the Director . The cholesteric mesophase is similar to the nematic it has long range order of the centre of mass of molecule it differs from the nematic mesophase the director varies throughout the medium in regular way even in unstrained state the director distribution is precisely or would be obtained by twisting a nematic aligned along the Y axis about the X axis.

The secondary structure of cholesteric is characterized by the distance measured along the X axis over which the director rotates through a full circle . This distance is called the **pitch** of the cholesteric ,The periodicity length of the Cholesteric is actually only a half of this distance.

Formally a nematic liquid crystal is a cholesteric of an infinite pitch . As a result there is no phase transition between nematic and cholesteric mesophase : nematic doped with enantiomorphic compound become cholesteric of long finite pitch.The molecule forming the cholesteric mesophase have distinct right and left handed forms.

A Cholesteric liquid crystal display (ChLCD) is a display containing a liquid crystal with a helical structure and which is therefore chiral. Cholesteric liquid crystals are also known as chiral nematic liquid crystals. They organize in layers with no positional ordering within layers , but a director axis which varies with layers. The variation of director axis tends to be periodic in nature. The period of this variation(the distance over which a full rotation of 360° is completed) is known as pitch, p .This pitch determines the wavelength of light which is reflected(Bragg Reflection). The technology is characterized by stable i.e. focal conic state(bright state). Displays based on this technology are called “bistable” and don’t need any power to maintain the information (zero power). Because of the reflective nature of the ChLCD, these displays can be perfectly read under sunlight conditions.

Examples of compounds known to form cholesteric phases are hydroxypropyl cellulose and cholesteryl benzoate. Some companies such as Chiral photonics , have begun to explore CLCs as the basis for photonic devices. A U.S. company , Kent Displays has developed “no power” Liquid crystals displays using polymer stabilized cholesteric liquid crystals, these are known as ChLCD screens. A drawback of ChLCD is their low refresh rate, especially at low temperatures.

1.5.1 Properties of Smectic Liquid Crystals.

- They exhibit finger print texture.
- These are formed from optically active compound.
- A group of molecule is oriented at an angle to the adjacent group of molecule such that the director takes a helical path as it travel through the liquid crystal just as nut is moved to screw.

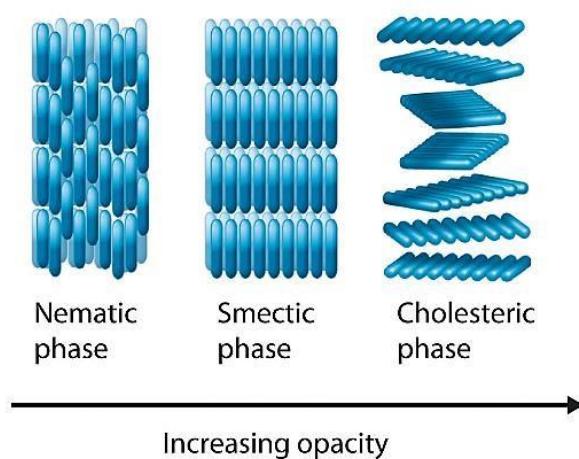


Figure 5 CHOLESTERIC LIQUID CRYSTALS w.r.t. opacity.

Image citation: <https://presschem.com/products/specialty-manufactured-products/liquid-crystals/>

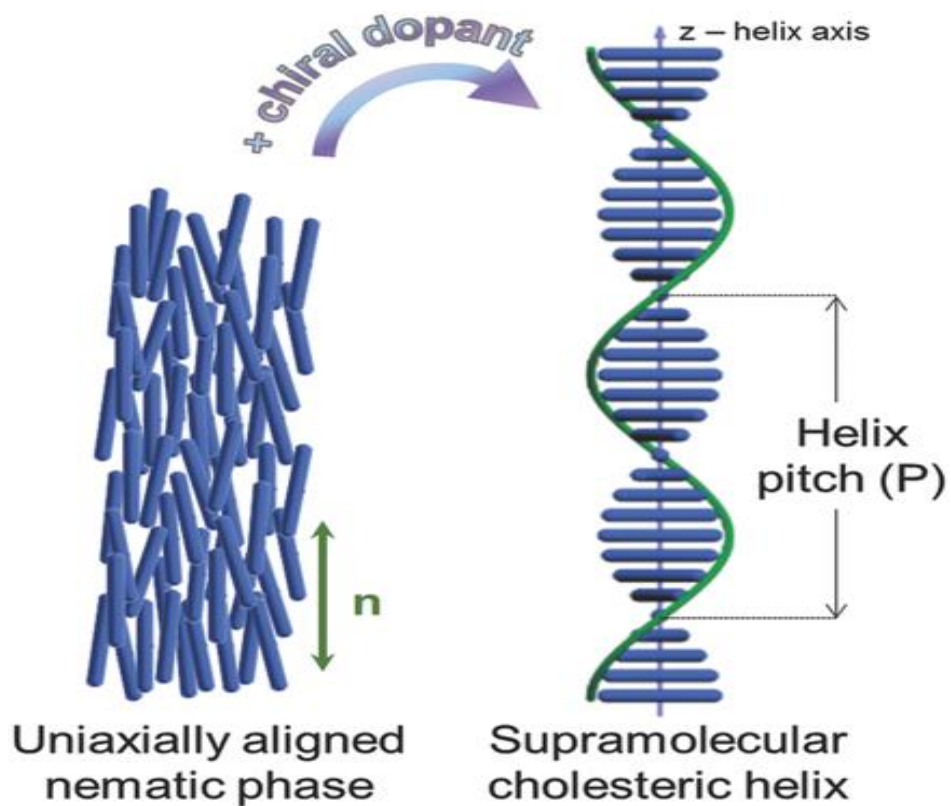
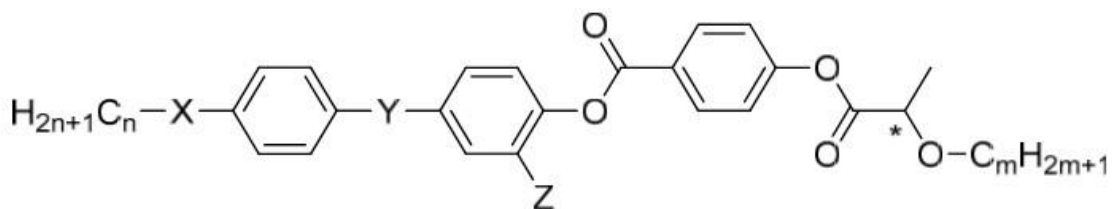


Figure 5 Demostration of helix pitch.

Image citation: <https://onlinelibrary.wiley.com/doi/10.1002/adom.201800335>

2. Material:

General structure of the investigated compound



Compound	n	M	X	Y	Z	Ref.
QM10\10	10	10	-O-	-COO-	H	[16]
QM12\9	12	9	-O-	-COO-	H	[16]
QM12\10	12	10	-O-	-COO-	H	[16]
E8\10	8	7	-OCO-	-OCO-	H	[14]
E6\10	6	10	-OCO-	-OCO-	H	[14]
E10\10	10	10	-OCO-	-OCO-	H	[14]
E8\12	8	12	-OCO-	-OCO-	H	[14]
QVE8\5	8	5	-O-	-OCO-	-OCH ₃	[15]

3. DIELECTRIC BEHAVIOUR :

3.1 Complex permittivity with Frequency dispersion:

The dielectric response is a useful experimental method to observe and investigate various molecular relaxation phenomena that may occur in FLC systems. The dielectric spectra, that is, the frequency dependent behaviour of the real (ϵ') and imaginary (ϵ'') part of complex permittivity at different temperatures in the SmC* phase for one representative **QM10/10** compound, has been shown in Figure 6a; analogous behaviour was observed in different FLC materials [17-23]. It has been obtained from the experimental data that the real as well as the imaginary part of complex permittivity increases with temperature upto about 393K [see Figure 6a]; then, with further increase of temperature, these values started to decrease. This may be due to the disruption in the orderly arrangement of the dipoles within the molecular domains as the SmC*–N* phase transition is approached. The real part of the permittivity (ϵ_0) decreases smoothly with frequency increase and becomes nearly constant in the higher frequency region. On the other hand, the imaginary part of the complex permittivity (ϵ'') shows a strong collective relaxation phenomenon related to the Goldstone mode (fluctuations of the long molecular axis in the azimuthal direction) in the SmC* phase, with the frequency range of about (1–10) kHz [17,22,23]. At higher frequency regime ϵ'' does not show much variation with frequency and becomes nearly constant as in ϵ_0 . In order to investigate the effect of the end alkyl chain length in both the chiral as well as non-chiral part on the dielectric spectra, we have plotted three **QMn/m** compounds differing in the lengths of the chiral and non-chiral alkyl chains [Figure 6b] in the SmC* phase. It has been observed that among all the three compounds of the **QMn/m** series, the **QM10/10** compound attained the highest values of both ϵ' and ϵ'' . This can be explained by the presence of same number of hydrocarbon groups in the chiral and non-chiral fragments of **QM10/10** compound, which gives rise not only to a symmetric configuration of the molecules but also decreases the rotational hindrance of the chiral part in comparison to the other two compounds. As a result, large number of molecules are aligned along a preferred direction, consequently increasing the permittivity.

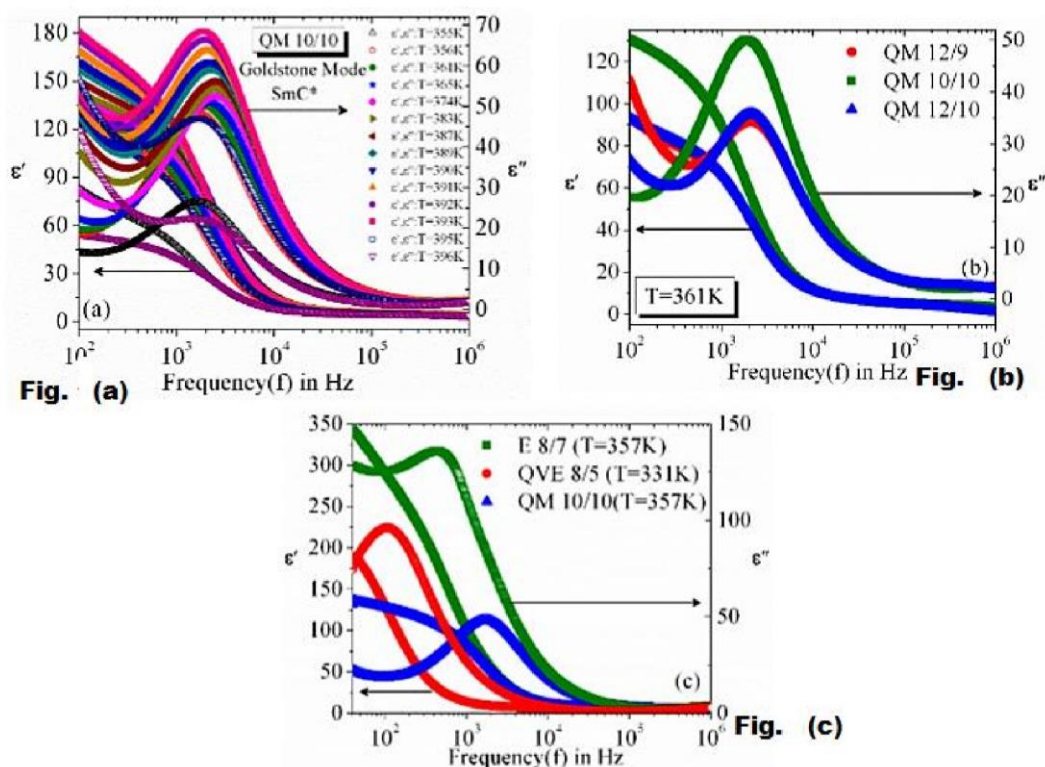


Figure 6. Frequency dependence of real (ϵ') and imaginary (ϵ'') part of complex permittivity in the ferroelectric SmC* phase for: (a) QM10/10 at different temperatures; (b) three of QMn/m compounds at $T=361K$ and (c) three structurally different QVE8/5($T=331K$), E8/7 ($T=357K$), QM10/10($T=357K$) compounds

To observe how the core structure of the constituent molecules affects the values of ϵ' and ϵ'' , we have chosen three structurally different compounds, namely **E8/7**, **QVE8/5** and **QM10/10**. It can be observed from Figure 6c that the **E8/7** compound has the largest ϵ' and ϵ'' values among the three: the additional dipoles originating from the carboxy group in this compound contributes towards this effect. Another noticeable fact is that the polar lateral methoxy group in QVEn/m series gives rise to larger values of ϵ' and ϵ'' than that for QMn/m series. Figure 7a shows the Cole–Cole plot for **QM10/10** compound at five different temperatures within the SmC* phase. Beyond the Goldstone mode detected at relatively low frequencies, a higher frequency process was found and is attributed to the finite resistivity of ITO layers in measuring cells (see in set of Figure 7a) [17,20,24]; within the SmC* phase the dielectric losses rise with temperature. It is necessary to mention that dielectric losses depend not only on the molecular core structure but also on the alkyl chain lengths. It has been observed that depending on the end alkyl chain length the dielectric loss (ϵ'') is different for different compounds (see Figure 7b). Figure 7c represents the Cole–Cole plot for three compounds taken from three structurally different series. It is clear from the Figure 7 that the dielectric loss is largest for the **E8/7** compound [19,20,24,25].

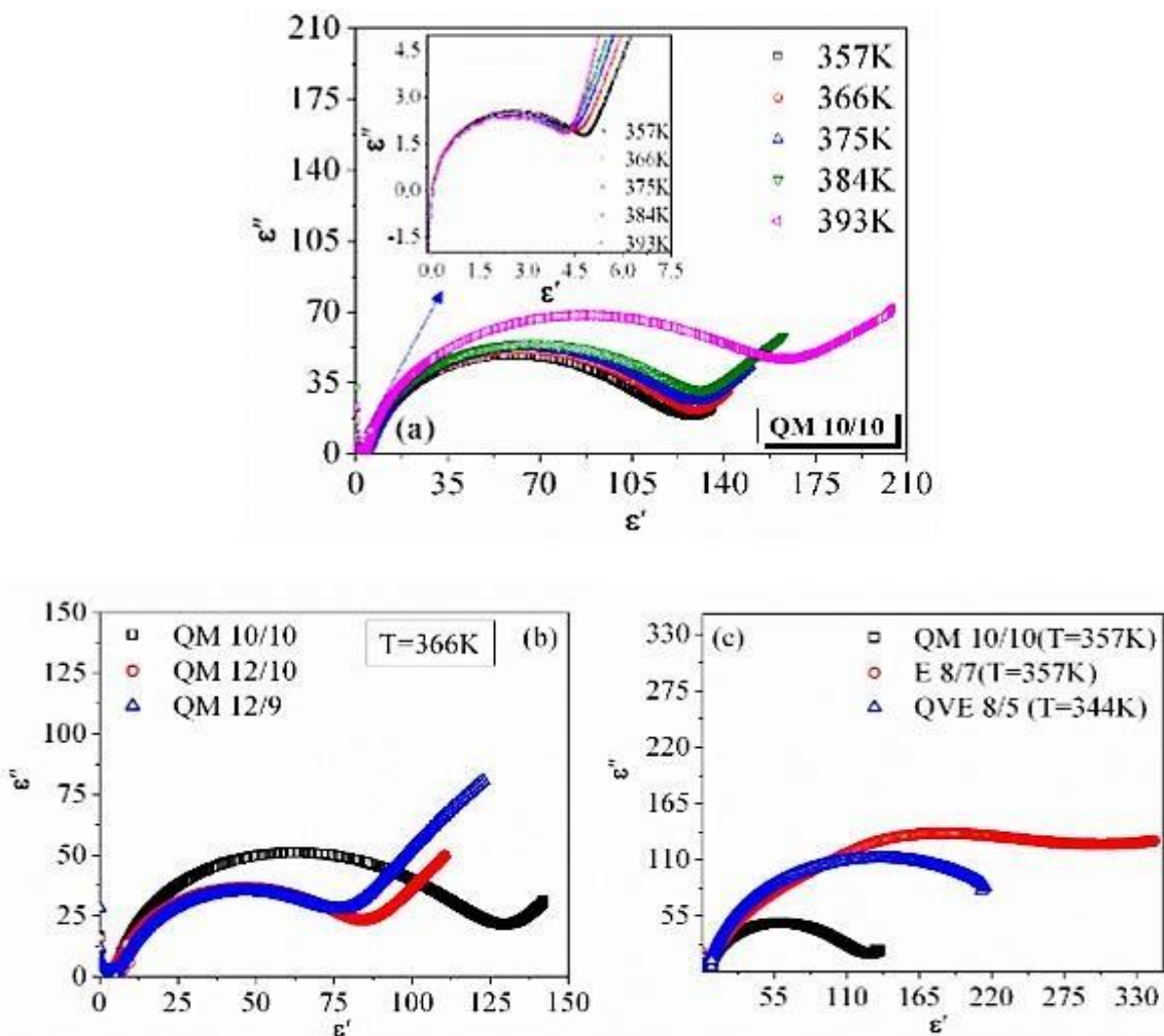


Figure 7. Cole–Cole plots for: (a) QM10/10 compound at five temperatures (as indicated) where the inset shows the high frequency contribution related to ITO electrodes; (b) three QMn/m compounds at $T = 366$ K; (c) three structurally different QVE8/5 ($T = 344$ K), E8/7 ($T = 357$ K), QM10/10 ($T = 357$ K) compounds.

In order to determine the relaxation mode parameters such as dielectric strength ($\Delta\epsilon$), relaxation time (τ_r), relaxation frequency (f_r) related to the maximum of loss peak, a logarithmic plot of the imaginary part of complex permittivity (ϵ'') versus frequency is shown in Figure 8a–c; the data were fitted by the Havriliak–Negami equation [26,27]. The logarithmic plot of imaginary part of complex permittivity at five different temperatures has been shown for one of the representative **QM10/10** compound [see Figure 8a]. The same figures has been plotted in the vicinity of the Cr–SmC* (at about $T = 366$ K) and SmC*–N* (at about $T = 396$ K) phase transitions for all the three compounds of the same homologous series QMn/m [see Figure 8b,c]. From these two figures it can be seen easily that the dielectric strength of relaxation mode considerably decreases in the temperature region very close to the N*–SmC* phase transition and it is more distinct for

QM10/10 compound; this effect can be explained by the possible helix unwinding phenomenon near the N*–SmC* phase transition.

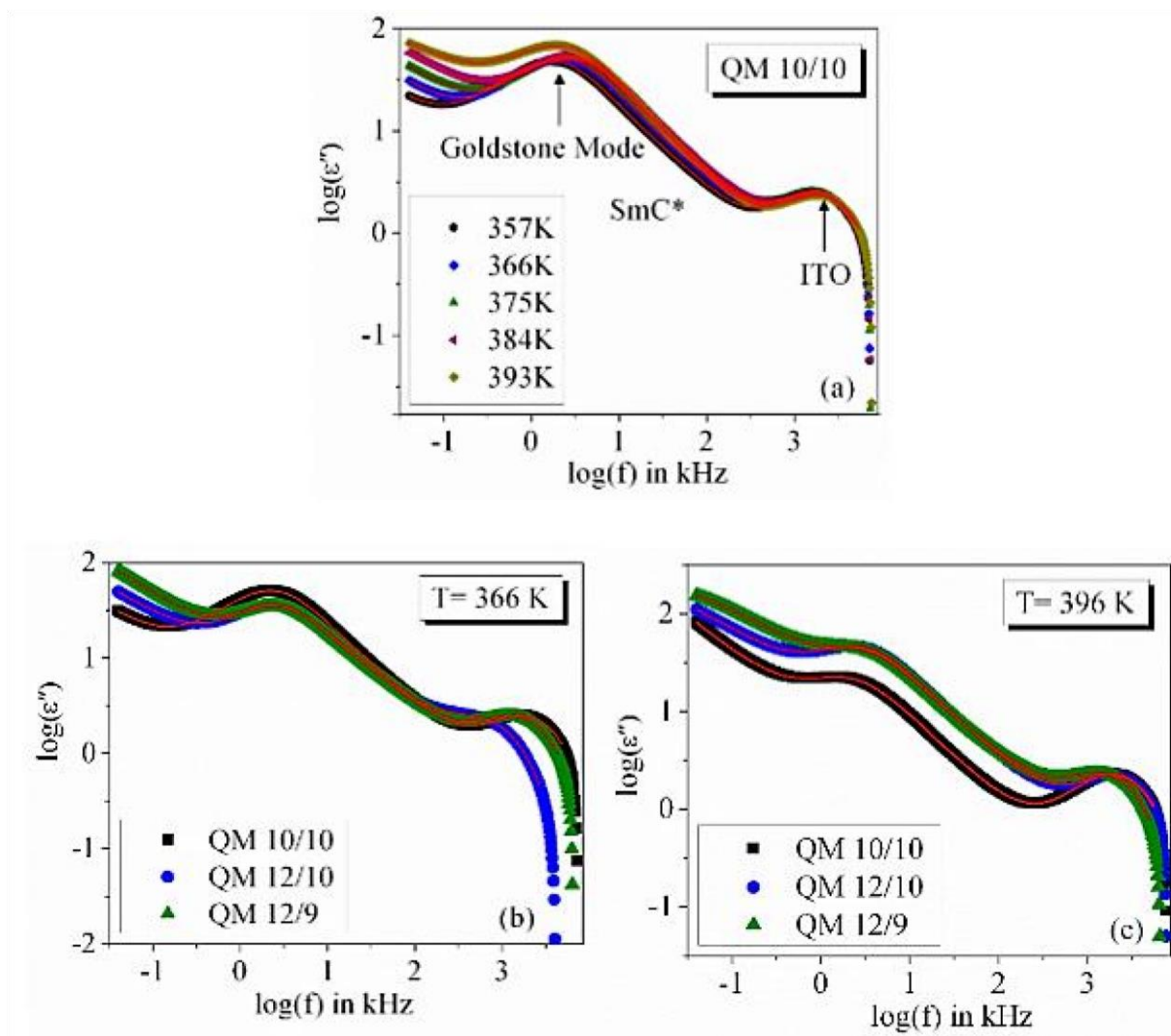


Figure 8. The Imaginary part of complex permittivity (ϵ'') for: (a) QM10/10 compound at five temperatures as indicated; (b) compounds from QMn/m series close to the Cr-SmC* phase transition at $T=366$ K; (c) compounds from QMn/m series close to the SmC*-N* phase transition at $T=396$ K; The red solid curves represent the results of fitting by Havriliak–Negami equation to the experiment.

3.2 Dielectric Strength and Relaxation Frequency Temperature Dependence:

Figure 9a, b represents the temperature dependence of the dielectric strength ($\Delta\epsilon$) (as a result of fitting procedure) for the studied compounds within the temperature range of the ferroelectric SmC^* phase. Generally, the dielectric strength increases with increasing temperature in the SmC^* phase (see Figure 9a,b), revealing a maximum close to the $\text{N}^*/\text{SmA}^*-\text{SmC}^*$ phase transition and then decreases abruptly with further increase in temperature. A similar effect has been observed by others [19,20,22,25].

One important observation is that **QM10/10** compound, possessing the same lengths of both chiral(**m**) and non-chiral(**n**) alkyl chains, exhibits the largest dielectric strength (about $\Delta\epsilon = 130$) among all the compounds from the **QMn/m** series. Values of $\Delta\epsilon$ are slightly smaller for **QM12/9** compound with respect to that of **QM12/10** compound. However, **E8/7** compound exhibits the largest dielectric strength among the three structurally different compounds as shown in Figure 4b, probably due to the presence of a second polar carboxylate group which can generate additional mobile charges, and hence can increase the total dipole moment.

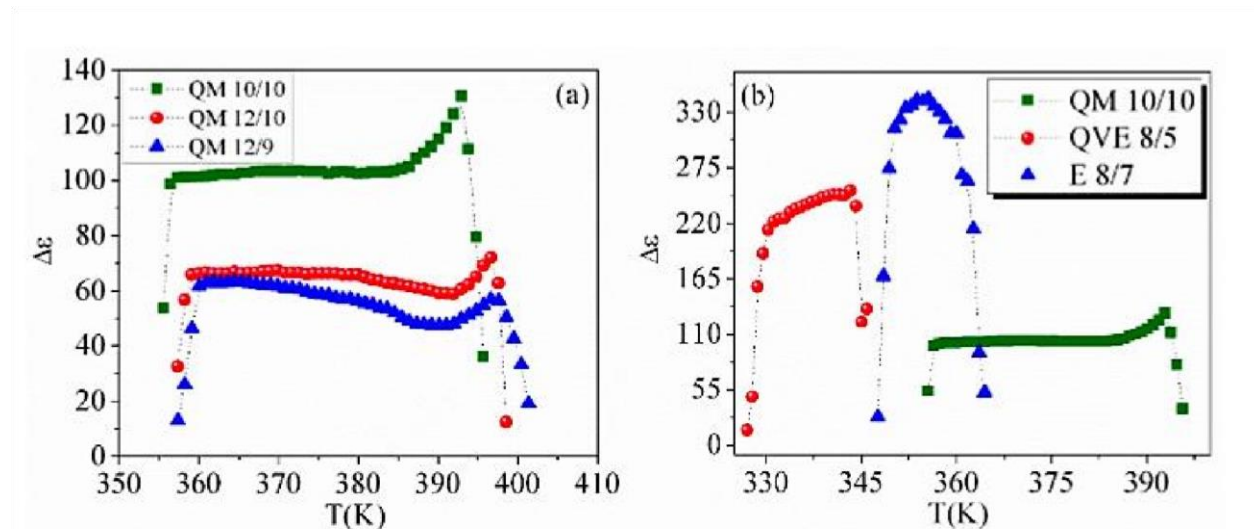


Figure 9. Temperature dependence of the dielectric strength ($\Delta\epsilon$) within the temperature range of the SmC^* phase for: (a) structurally similar **QMn/m** compounds differing only in the length of the terminal alkyl chains; (b) structurally different **QVE8/5**, **E8/7** and **QM10/10** compounds.

The temperature dependence of relaxation time and relaxation frequency for **QMn/m** series is shown below

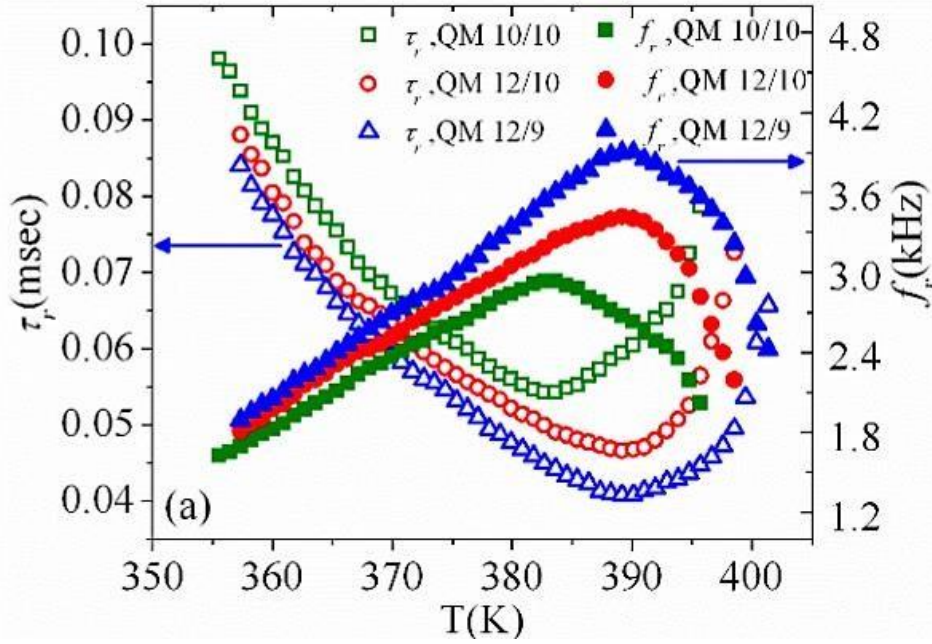


Figure 10 (a) Temperature dependence of relaxation time and relaxation frequency of the Goldstone mode for three QMn\m compounds

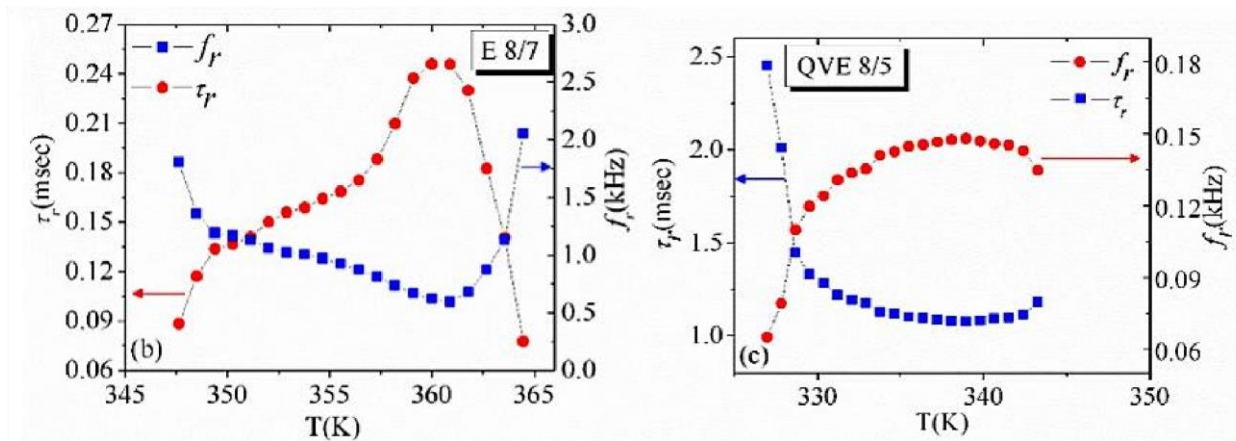


Figure 10 Temperature dependence of relaxation time and relaxation frequency of the Goldstone mode for (b) E8\7 compound; (c) QVE8\5 compound.

The Goldstone mode contributions attributes towards an enhanced relaxation frequency with temperature within the SmC* phase: these values rise, attain a maximum and then starts to decrease about 10 K below the N*–SmC* phase transition [28,29], perhaps due to the consequent decrease of ferroelectricity near the SmA*/N*–SmC* phase transitions. Among all three **QMn/m**

compounds, the **QM10/10** one exhibits the lowest relaxation frequency that attains its maximum value at the low temperature region in comparison with another two possessing different lengths of chiral and non-chiral terminal alkyl chains. Moreover, the temperature dependence of the relaxation time has an inverse nature in relation to the relaxation frequency [28-30]. Temperature dependence of the relaxation time and relaxation frequency for **E8/7** and **QVE8/5** compounds are shown in Figure 10b,c, respectively. It may be noted that the temperature dependence of the relaxation frequency in the SmC* phase for **QVE8/5** and **QMn/m** compounds shows a similar trend; however, for **E8/7** the behaviour is quite different; first it decreases slightly, then increases with increasing temperature. This anomaly is probably due to an additional polar ester linking group (placed in between the non-chiral alkyl chain and the molecular core), which causes larger dipole moment and their repulsive interaction accounts for increase of relaxation time with increasing temperature. However, the ferroelectric dipolar coupling rapidly diminishes as the N*/SmA*–SmC* phase transition is approached, leading to a consequent decrease of the mutual repulsive interaction which now facilitates quick relaxation process with further increase of temperature. If we compare the values of relaxation frequency (f_r) and relaxation time (τ_r) it can be observed that compound belonging to **QVEN/m** series exhibits larger relaxation time and smaller relaxation frequency due to its relatively high viscosity caused by the presence of the lateral methoxy substitution on the central aromatic ring of the molecular core. Materials from **QMn/m** series possess smaller relaxation time and larger relaxation frequency due to its more flexible “zigzag shaped” molecular structure. On the other hand, f_r and τ_r values for materials from **En/m** series are intermediate with respect to the materials mentioned above. Thus, for the studied ferroelectric liquid crystalline materials, it can be concluded that the parameters of the relaxation mode strongly depend on both the molecular core structure and alkyl chain lengths.

4. Discussion of Results:

The ferroelectric SmC* phase for the compounds belonging to three structurally different series of chiral self-assembling compounds possessing the ferroelectric polar order has been investigated via broadband dielectric spectroscopy measurements. The behaviour of dielectric spectra not only depends on the temperature but also on the specific molecular structure of the FLC compounds. The results of the investigations lead to the following summary.

Within the SmC* phase, both real and imaginary parts of complex permittivity increase upto certain temperature then drop with increasing temperature. The length of the alkyl chains length as well as linkage unit has a great influence on the values of the dielectric permittivities.

The real (ϵ') and imaginary (ϵ'') parts of the complex dielectric permittivity as well as the dielectric losses (ϵ''/ϵ') are maximum for **En/m** series and minimum for **QMn/m** series; this is attributed due to polar nature of the ester connecting group (situated in between the non-chiral alkyl chain and the molecular core) which is present in the **En/m** series; this additional ester linkage group is present only for the **En/m** series.

By fitting of the experimental data for the imaginary part of the complex permittivity by the Havriliak–Negami equation, the dielectric strength ($\Delta\epsilon$) and relaxation frequency (f_r) of the Goldstone mode has been determined.

The temperature dependence of dielectric strength shows that $\Delta\epsilon$ increases with increasing temperature in the SmC* phase and attains a maximum value then decreases near the phase transition to the SmA*/N* phase.

The dielectric strength is also influenced by the difference of the alkyl chain length and type of linkage group of the constituent chiral molecules. It has been observed experimentally that the dielectric strength is maximum for **En/m** series and minimum for **QMn/m** series.

With increasing temperature, the relaxation frequency of the Goldstone mode shifts towards higher frequency region and attains a maximum at a certain temperature, then starts to decrease close to the phase transition to the SmA*/N* phase which appears at high temperatures.

It has been observed that the relaxation time (τ_r) and the relaxation frequency (f_r) varies with the molecular structure of the studied ferroelectric compounds. The value of τ_r is maximum for **QVEn/m** series and minimum for **QMn/m** series, due to the bulky methoxy ($-\text{OCH}_3$) group used as substituent in the lateral position on the middle aromatic ring of the **QVEn/m** molecules.

5. Conclusion:

Finally, it can be concluded that the dielectric parameters of the studied materials are considerably influenced by the specific variations of the molecular structure as it has been described. The conducted studies should contribute towards a better understanding of the structure–property correlations for these specific classes of soft organic self-assembling materials derived from the lactic acid which may be utilized for further design of new liquid crystalline mixtures aimed for advanced optoelectronic and photonic applications.

REFERENCES :

1. Schadt M. and W. Helfrich, Appl. Phys. Lett. 18, 127 ,1971
2. Waters C. M., E. P. Raynes, and V. Brimmell, Mol. Cryst. Liq. Cryst. 123, 303, 1985.
3. Scheffer T. J. and J. Nehring, Appl. Phys. Lett. 45, 1021,1984
4. Meyer R. B., Fifth International Liquid Crystal Conference, Stockholm, 17–21 June 1974 unpublished
5. Meyer R. B., L. Lieber, L. Strzelecki, and P. Keller, J. Phys. Paris, Lett. 36, L-69 1975.
7. Castillo P. L., J. Otón, R. Dabrowski, A. Lara, X. Quintana, and N. Bennis, Proc. SPIE 5565, 284,2004.
8. Quintana X., P. L. Castillo, J. Otón, N. Bennis, A. Lara, and R. Dabrowski, Proc. SPIE 5565, 290,2004.
9. Dabrowski R., K. Czuprynski, J. Gasowska, J. Oton, X. Quintana, P. L. Castillo, and N. Bennis, Proc. SPIE 5565, 66,2004.
10. D’have K., Ph.D. thesis, University of Gent, 2001.
11. Lagerwall,S. T. Ferroelectric and Antiferroelectric Liquid Crystals ,Wiley, Weinheim, 1999.
12. Rudquist P., J. P. F. Lagerwall, J. G. Meier, K. D’have, and S. T. Lager- wall, Phys. Rev. E 66, 061708 2002.
13. Lagerwall S., A. Dahlgren, P. Jagemalm, P. Rudquist, K. D’have, H. Pau- wels, R. Dabrowski, and W. Drzewinski, Adv. Funct. Mater. 11, 87 2001.
14. Pakhomov, S.; Kaspar, M.; Hamplova, V.; Bubnov, A.; Sverenyak, H.; Glogarova, M.; Stibor, I. Synthesis and mesomorphic properties of (S)-lactic acid derivatives containing several ester linkages in the core. Ferroelectrics 1998, 212, 341–348.
15. Bubnov,A.; Kaspar,M.;Novotna,V.; Hamplova,V.;
Glogarova,M.;Kaperbaum,N.; Giesselmann,F.Effectof lateral methoxy substitution on mesomorphic and structural properties of ferroelectric liquid crystals. Liq. Cryst. 2008, 35, 1329–1337.
16. Vajda, A.; Kaspar, M.; Hamplova, V.; Pakhomov, S.A.; Vanek, P.; Bubnov, A.; Csorba, K.F.; Éber, N. Synthesis and liquid crystalline properties of (S)-[4-

- nAlkyloxy-benzoyloxyphenyl]-40[(2-nalkyloxy)propionyloxy]benzoate. *Mol. Cryst. Liq. Cryst.* 2001, 365, 569–580.
17. Shukla, R.K.; Raina, K.K.; Hamplová, V.; Kašpar, M.; Bubnov, A. Dielectric behaviour of the composite system: Multiwall carbon nanotubes dispersed in ferroelectric liquid crystal. *Phase Transit.* 2011, 84, 850–857.
 18. Mishra, A.; Wegłowska, D.; Dabrowski, R.; Dhar, R. Relaxation phenomena of a highly tilted ferroelectric liquid crystalline material (S)-(+)-40-(3-pentanoyloxy prop-1-oxy)biphenyl-4-yl-4-(1-methylheptyloxy)benzoates. *Liq. Cryst.* 2015, 42, 1543–1549.
 19. Pandey, M.B.; Dhar, R.; Dabrowski, R. Dielectric spectroscopy of a newly synthesized chlorinated analogue of MHPOBC antiferroelectric liquid crystals. *Ferroelectrics* 2006, 343, 83–100.
 20. Kaur, S.; Dierking, I.; Gleeson, H.F. Dielectric spectroscopy of Polymer Stabilized Ferroelectric Liquid Crystals. *Eur. Phys. J. E* 2009, 30, 265–274. [PubMed]
 21. Dwivedi, A.; Dhar, R.; Dabrowski, R. Dielectric Spectroscopy of Para-, Ferro-, and Anti-Ferro-Electric Phases of (S)-(+)-(1-Methylheptyloxycarbonyl)Phenyl40-(6-Perfluoropentanoyloxyhex-1-Oxy)Biphenyl-4-Carboxylate. *Soft Mater.* 2009, 7, 54–65.
 22. Dhar, R.; Singh, S.; Das, I.M.L.; Dabrowski, R. Thermodynamic and dielectric studies of liquid crystalline compound (S)-(+)-4-(1-methylheptyloxycarbonyl)phenyl 40-(6-octanoyloxyhex-1-oxy) biphenyl-4-carboxylate. *Phase Trans.* 2009, 82, 251–265.
 23. Gupta, S.K.; Singh, D.P.; Manohar, R. Enhancement of Dielectric and ElectroOptical Properties in SWCNT Dispersed Ferroelectric Liquid Crystals. *Ferroelectrics* 2014, 468, 84–91.
 24. Perkowski, P. Dielectric spectroscopy of liquid crystals, theoretical model of ITO electrodes influence on dielectric measurements. *Opto-Electron. Rev.* 2009, 17, 180–186.
 25. Wojciechowski, M.; Gromiec, L.A.; Bak, G.W. Dielectric characteristics of chiral smectic C sub phases in liquid crystal MHPOPb. *J. Mol. Liq.* 2006, 124, 7–12.

26. Havriliak, S., Jr.; Negami, S. A Complex plane analysis of α -dispersions in some polymer systems. *J. Polym. Sci. C* 1966, 14, 99.
27. Kundu, K.S.; Yagihara, S.; Yoshizawa, A. Dielectric spectroscopy of a smectic liquid crystal. *Liq. Cryst.* 2007, 34, 981–986.
28. Manohar, R.; Yadav, S.P.; Pandey, K.K.; Srivastava, A.K.; Misra, A.K. Comparative study of dielectric and electro-optical properties of pure and polymer ferroelectric liquid crystal composites. *J. Polym. Res.* 2011, 18, 435–441. *Crystals* 2019, 9, 473 13 of 13
29. Srivastava, A.K.; Manohar, R.; Shukla, J.P.; Biradar, A.M. Dielectric relaxation of dye-doped ferroelectric liquid crystal mixture: A comparative study of Smectic C* and Smectic A phase. *Jpn. J. Appl. Phys.* 2007, 46, 1100–1105. [CrossRef]
30. Pandey, M.B.; Dhar, R.; Dabrowski, R. Electrical characteristics of wide temperature range phase. *Mol. Cryst. Liq. Cryst.* 2009, 509, 363–377.
31. Kurp, K.; Tykarska, M.; Salamon, P.; Czerwinski, M.; Bubnov, A. Design of functional multicomponent liquid crystalline mixtures with nano-scale pitch fulfilling deformed helix ferroelectric mode demands. *J. Mol. Liq.* 2019, 290, 111329
32. Fitas, J.; Marzec, M.; Szymkowiak, M.; Jaworska Goła b, T.; Deptuch, A.; Tykarska, M.; Kurp, K.; Zurowska, M.; Bubnov, A. Mesomorphic, electro-optic and structural properties of binary liquid crystalline mixtures with ferroelectric and antiferroelectric liquid crystalline behavior. *Phase Trans.* 2018, 91, 1017–1026.
33. Fitas, J.; Marzec, M.; Kurp, K.; Zurowska, M.; Tykarska, M.; Bubnov, A. Electrooptic and dielectric properties of new binary ferroelectric and antiferroelectric liquid crystalline mixtures. *Liq. Cryst.* 2017, 44, 1468–1476.
34. Bubnov, A.; Podoliak, N.; Hamplová, V.; Tomašková, P.; Havlíček, J.; Kašpar, M. Eutectic behaviour of binary mixtures composed by two isomeric lactic acid derivatives. *Ferroelectrics* 2016, 495, 105–115.
35. Kurp, K.; Czerwinski, M.; Tykarska, M.; Bubnov, A. Design of advanced multicomponent ferroelectric liquid crystalline mixtures with sub-micrometer helical pitch. *Liq. Cryst.* 2017, 44, 748–756.
36. Sreenilayam, S.P.; Brabazon, D.; Panarin, Y.P. Fast ferroelectric liquid crystal based optical switch: Simulation and experiments. *Crystals* 2019, 9, 388.
37. Dabrowski R.; Kula, P.; Herman, J. High Birefringence Liquid Crystals. *Crystals* 2013, 3, 443–482

