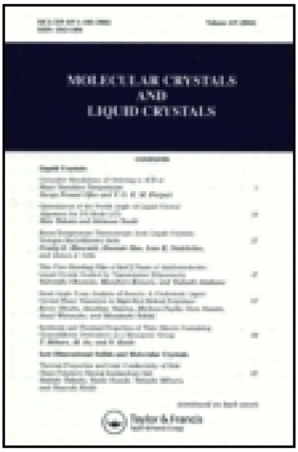

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Dielectric Characterisation of an Orthoconic Antiferroelectric Liquid Crystal Mixture

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Dielectric properties of the orthoconic smectic liquid crystalline mixture W-129, which presents both antiferroelectric and ferroelectric smectic C phases, have been studied in the frequency range from 10 mHz to 100 kHz in planar aligned cells. Some important relaxation modes were detected in SmCa and SmC* phases. Dielectric increments, distribution parameters and relaxation frequencies of these modes have been evaluated at different temperatures. From the study of dielectric spectra a great variety of relaxation responses emerges that could indicate the presence of different SmCa* subphases.*

Keywords Dielectric spectroscopy; orthoconic antiferroelectric mixtures; relaxation modes

Introduction

It is well known that tilted chiral structures in smectic liquid crystal phases exhibit spontaneous polarization and if the structure is synclinic the liquid crystal is called ferroelectric liquid crystal (FLC) while if the structure is anticlinic (the director is tilted in opposite direction in alternate layers) the liquid crystal is an antiferroelectric liquid crystals (AFLC).

The study of FLCs and AFLCs is important for different aspects: the interesting physical properties and their application in electro-optical devices. Moreover, due to their fast response time, they can be employed in visual display applications [1,2].

Dielectric spectroscopy is a useful tool for characterizing liquid crystals phases which allows a temperature dependent analysis of their physical properties.

The electro-optical response of a liquid crystal cell is related to dielectric modes observed in liquid crystals phases. In fact if the dielectric relaxation mode is fast, the electrooptical switching related to this mode can be fast as well [3].

If a smectic C* (SmC*) phase is present in the Liquid Crystal (LC) phase diagram, the dielectric response would be a result of two relaxation modes [4–7]. The first, Goldstone mode, due to the phase fluctuation in the azimuthal orientation of the director, is usually observed in the low frequency range. The second is the soft mode that corresponds to

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fluctuations in the tilt-angle of the director and appears in the SmC* and in the SmA* phases becoming more evident near SmC* to SmA* phase transition.

In this work, dielectric spectroscopy is used to investigate the high-tilted chiral smectic phases of the antiferroelectric liquid crystal W-129. This material exhibits an high spontaneous polarization at room temperature (300 nC/cm^2) in virtue of its tilted chiral structure (the tilt angle is 45° at room temperature). The Cole-Cole function has been used to determine the dependence of distribution parameter, dielectric increment (also called dielectric strength) and relaxation frequency as a function of temperature.

Experimental

W-129 has been synthesized from R. Dabrowski group at the Military University of Technology, in Warsav, Poland, it is a smectic liquid crystalline mixture which presents both ferroelectric and antiferroelectric smectic C phases. The phase sequence of this material is the following: Cr - 13/15°C - SmCa* - 84.5°C - SmC* - 102.3°C - SmA* - 117/125.2°C Iso, obtained from DSC measurements. The study of electro-optical properties of W-129 has been already done in the past as detailed in Ref. [8].

A Japanese commercial cell (EHC Ltd, Tokyo, Japan) with a thickness of (2.0 ± 0.2) μm and a ITO resistance of 100 $\Omega/\square$ has been used. The cell was filled by capillary method in the isotropic phase [9].

The dielectric measurements have been carried out using an EG&G 263A galvanostat-potentiostat in the frequency range 10 mHz–100 kHz with a maximum applied voltage of 0.5 V (RMS) and no bias field was applied. In order to perform dielectric measurements as a function of temperature the sample has been placed in a CaLCTec FB150 programmable temperature hot stage, it has been slowly heated to a temperature of 110°C and then slowly cooled in order to achieve the best conditions for dielectric measurements.

Results and Discussion

The real part of the dielectric permittivity (ε^I) is almost constant in the SmA* phase and for frequencies from 0.1 to 10 Hz (see Fig. 1). For these frequencies, ε^I is also almost constant in the SmC* phase. For the other frequencies the real part of the permittivity decreases gradually with decreasing temperature until the SmA*-SmC* transition temperature is reached, then it increases slowly for frequencies equal to 100 Hz and 10 kHz and increases rapidly for frequency equal to 1 kHz. In this last region the soft ferroelectric mode contributes to the increase of the dielectric constant.

Further cooling the sample, below the SmC*- SmCa* transition, the dielectric constant decreases slowly till the temperature of 70°C is reached, then decreases very rapidly. The measurements performed at 10 kHz show an opposite behaviour.

The frequency dependence of the real and imaginary parts of the dielectric constant, respectively called, dispersion and absorption or dielectric loss curve, shows different relaxation responses (see Fig. 2(a),(b)). The dielectric loss curve (Fig. 2(b)) shows a very high relaxation peak, probably due to the ionization diffusion in the limit of zero mobility of slow ions at room temperature (20/25°C) and at very low frequencies (~0.1 Hz). The Goldstone mode results more evident in the region from 10 to 10^2 Hz and for temperatures from 85°C to 110°C.

For a complete overiew of experimental data, dispersion/absorption spectra are shown together with the Cole-Cole plots obtained for every fixed temperature. All parameters

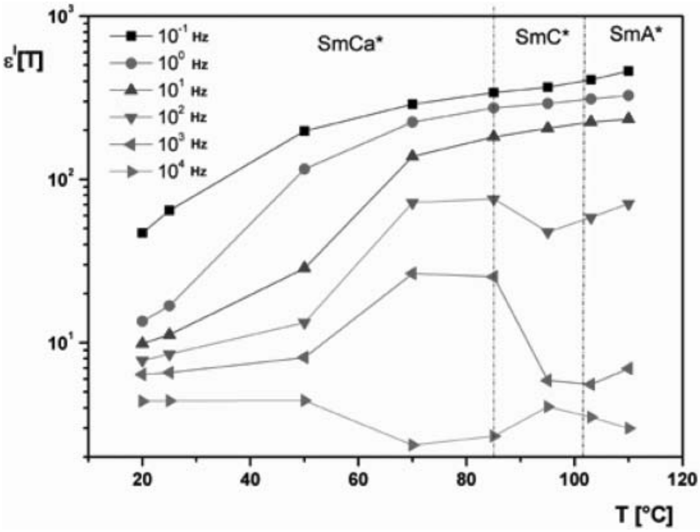

Figure 1. Temperature dependence of the real part of the dielectric constant at different fixed frequencies.

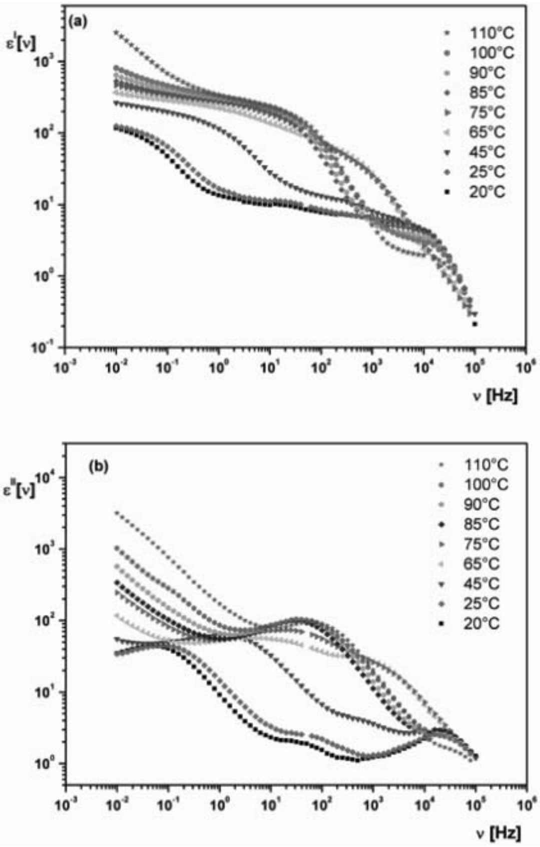

Figure 2. Dispersion (a) and absorption (b) curves of the dielectric spectra acquired for W-129 at different temperatures.

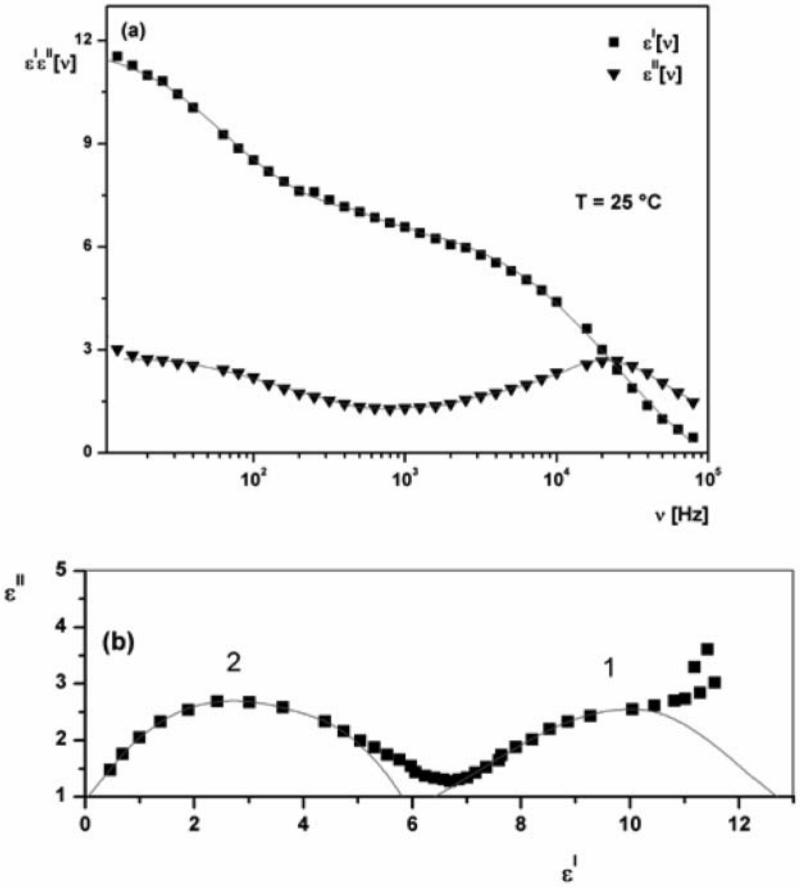

Figure 3. Dispersion and absorption curves (a) and Cole-Cole plot (b) of the dielectric spectra acquired for W-129 at 25°C. The solid red line shows the best theoretical fit of the Cole–Cole equation into experimental data.

were obtained from fitting the experimental dielectric constant data with the Cole-Cole modification of the Debye equation [10],

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon(0) - \varepsilon_\infty}{1 + (i2\pi\upsilon\tau)^{1-\alpha}} \tag{1}$$

Table 1. Fitting parameters for the two relaxation processes shown in Fig. 3 for SmCa* phase of W-129

T = 25°C						
Process	f_a	ε (0)	τ [s]	α	ε (∞)	$\Delta\varepsilon$
1	63.47	11.84	2.51 · E ^−3	0.31	6.78	5.06
2	2.38 · E ^+4	6.79	6.68 · E ^−6	0.49	1.59	5.20

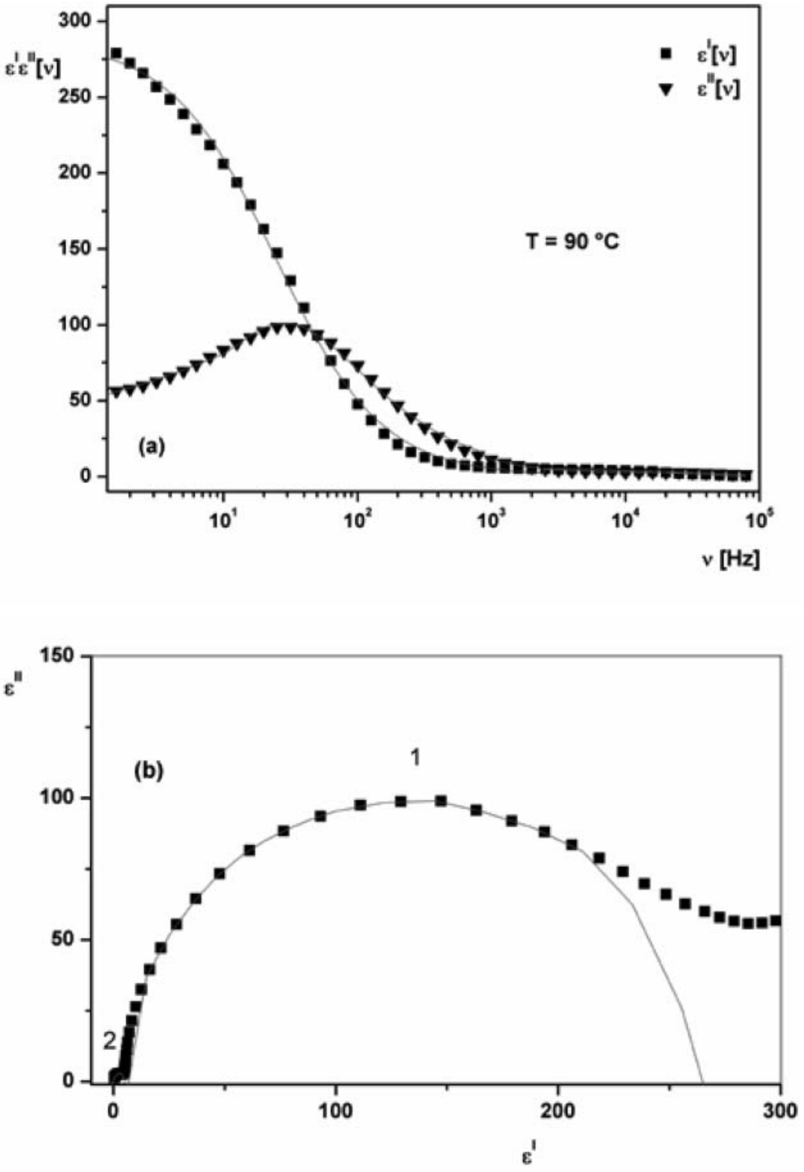

Figure 4. Dispersion and absorption curves (a) and Cole-Cole plot (b) of the dielectric spectra acquired for W-129 at 90°C. The solid red line shows the best theoretical fit of the Cole–Cole equation into experimental data.

where v is the frequency, $\varepsilon(0)$ is the static dielectric constant, ε_∞ is the high frequency dielectric constant, $\tau(=1/(2\pi v_a))$ is the dielectric relaxation time, v_a is the absorption peak frequency and α is the distribution parameter for a particular relaxation process that varies between 0 and 1. If α is very small (eq. 1), it satisfies the Debye equation while if α is more than 0.5 there could be more than one relaxation process.

Table 2. Fitting parameters for the two relaxation processes shown in Fig. 4 for SmC* phase of W-129

T = 90°C						
Process	f_a	ε (0)	τ [s]	α	ε (∞)	$\Delta\varepsilon_i$
1	24.42	287.42	6.52 · E ^−3	0.45	0.67	286.75
2	2.28 · E ^+4	5.05	6.98 · E ^−6	0.08	0.12	4.93

The real and imaginary part of the dielectric constant are shown together with the Cole-Cole plots at 25°C and 90°C respectively (see Fig. 3 and Fig. 4).

The relaxation response of W-129 at 25°C (Fig. 3(b)) is typical of the antiferroelectric phase. Two relaxation processes are evident: the relaxation process (2) corresponds to Anti-phase mode (PHM), the other process (1) corresponds to In-phase mode (PLM). In the Cole-Cole plot, obtained at 90°C (Fig. 4(b)), the Goldstone mode is well clear (1), while the Soft mode (2) is weakly detected.

The large value of distribution parameters evalueted for both processes at 25°C (see Table 1) makes the Cole-Cole plot far from being a overlapping of two semi-circles. The same result has been obtained for process (1) at 90°C (see Table 2) where an unusually large value of dielectric increment has been revealed. The very small value of the distribution parameter for process (2) (Table 2) makes the Cole-Cole mode very close to be a semi-circle, reducing it to a Debye response.

Conclusions

The basic physical parameters (i.e. relaxation frequencies, relaxation times, dielectric increments and distribution parameters) of an antiferroelectric liquid crystalline mixture have been determined for SmCa* and SmC* phases.

From dielectric spectra a great variety of relaxation responses that could indicate the presence of different SmCa* subphases is observed. Contributions to permittivity arise principally from the Goldstone mode and, in particular, dielectric increment is very large (~287). A very high relaxation peak, probably due to the ionization diffusion in the limit of zero mobility of slow ions, is also present at low temperatures (20/25°C) and at low frequencies (~0.1 Hz).

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