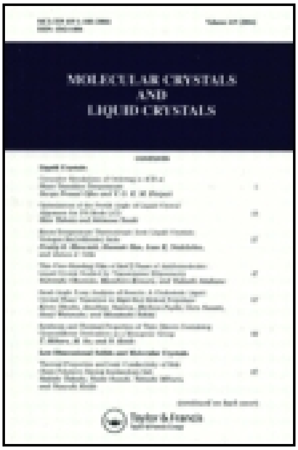


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Study of the SmCa * phase by dielectric measurements

J. Rutkowska [a] , P. Perkowski [a] , J. Kędzierski [a] , Z. Raszewski [a] , S. Kłosowicz [a] , R. Dąbrowski [b] , K. Czupryński [b] & S. Gauza [b]

[a] Institute of Applied Physics, Military University of Technology, Poland

[b] Institute of Chemistry, Military University of Technology, Poland

Version of record first published: 18 Oct 2010

To cite this article: J. Rutkowska, P. Perkowski, J. Kędzierski, Z. Raszewski, S. Kłosowicz, R. Dąbrowski, K. Czupryński & S. Gauza (2004): Study of the SmCa * phase by dielectric measurements, Molecular Crystals and Liquid Crystals, 409:1, 389-400

To link to this article: http://dx.doi.org/10.1080/15421400490433730

Mol. Cryst. Liq. Cryst., Vol. 409, pp. 389–400, 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490433730

STUDY OF THE SmC_α^* PHASE BY DIELECTRIC MEASUREMENTS

J. Rutkowska, P. Perkowski, J. Kędzierski. Z. Raszewski, and S. Kłosowicz
Institute of Applied Physics, Military University of Technology, 00-908 Warsaw, Poland

R. Dąbrowski, K. Czupryński, and S. Gauza
Institute of Chemistry, Military University of Technology, 00-908 Warsaw, Poland

The aim of our work was to make precise dielectric measurements to confirm the existence of the SmC_α^* phase in non-fluorinated compound 2 and in bicomponent mixtures composed of compounds 2 and 1 with partially fluorinated terminal chain. From the linear temperature dependences of relaxation frequency f_R and the inverse dielectric strength $\Delta\varepsilon^{-1}$ obtained by fitting experimental values $\varepsilon'_\perp$ and $\varepsilon''_\perp$ to the Cole-Cole equation, the SmC_α^* phase was detected in compound 2 and the mixture of 0.9 mole fraction of compound 2 due to the changes of the slopes observed at $SmA \Rightarrow SmC_\alpha^*$ and $SmC_\alpha^* \Rightarrow SmC^*$. C^*. The relaxation processes observed in the SmC_α^* phase of investigated systems are strongly modified under bias, thus they are probably connected with the ferroelectric-like structure of this phase.

Keywords: Cole-Cole equation; dielectric measurements; SmC_α^* phase

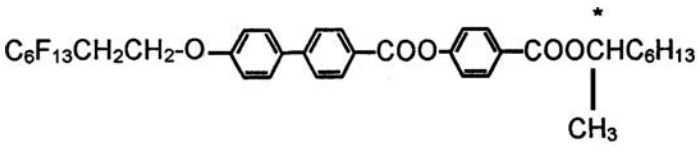
INTRODUCTION

Because of the structure of SmC_α^* phase is not clear so far, the experimental studies of this phase are still interesting. We have studied dielectric properties of this phase as a function of temperature and DC bias field to obtained better understanding of it.

This work has been supported by the State Committee for Scientific Research (MUT Statutory Task PBS 637).

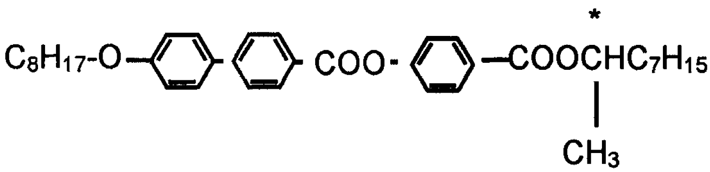
Address correspondence to J. Rutkowska, Institute of Applied Physics, Military University of Technology, Warsaw 00-908, Poland.

As the studied compounds have been chosen the following three ring chiral esters with partially fluorinated terminal chain (compound 1)



(S)

having the phase transitions: Cr 98.9 SmC* 150.4 SmA 184.4 Iso and hydrogenous analogue (compound 2)



(S)

with the following sequence of phases:

$Cr_1$60.8 Cr 79.7 (SmI_A*65.8) SmC*118.4 SmC_α*118.7 SmA 144.1 Iso.

Two bicomponent mixtures composed of compound 1 with 0.15 and 0.9 of molar fraction of compound 2, named by us mixture 1:2(0.15) and mixture 1:2(0.90), respectively, were investigated also. Both compounds and their mixtures have been extensively studied by us [1–3]. Results of spontaneous polarization, tilt angle in the SmC* phase and first dielectric permittivity measurements of all phases of compound 1 and compound 2 were presented by us in [1,2]. The existence of SmC_α* in non-fluorinated compound 2 and in bicomponent mixtures of these compounds in the concentration range above 0.3 molar fraction of compound 2 has found confirmation in DSC measurements [3]. These mixtures are very interesting from research and application point of view because of an appearance of induced antiferroelectric phase SmC_A* was observed in these [3].

EXPERIMENT

Dielectric measurements were performed in the frequency range from 50 Hz to 1 MHz with HP4192A impedance analyser. DC bias voltage up to 30 V was superimposed to the measuring AC voltage 0.1 V applied perpendicularly to the helical axis, i.e. parallel to the smectic layer, so perpendicular components: real $\varepsilon_\perp'$ and imaginary $\varepsilon_\perp''$ parts of the complex dielectric permittivity were studied. The temperature of cells (the commercially available EHC cells of thickness about 7 μm) placed inside the Linkam THMS600 hot stage was controlled by the Linkam TMS91 controller with an accuracy of 0.1 K. Similar results of dielectric measurements were obtained on cooling and on heating for all investigated system, except of mixture 1:2(0.90). Thus we are presenting only experimental data on cooling. In mixture 1:2(0.90) due to labile system well-known large hysteresis of temperature between ferroelectric and antiferroelectric transition occurs during heating and cooling cycles [2,3]. But now we focussed our attention on different transitions, especially for phase transitions SmA $\Rightarrow$ SmC$_\alpha$* and SmC* $\Rightarrow$ SmC$_\alpha$*.

The dielectric strength $\Delta\varepsilon$, relaxation frequency f_R and dispersion parameter β were determined by fitting the dielectric data to the well-known Cole-Cole distribution:

$$\varepsilon_\perp^* = \varepsilon'_\perp - i\varepsilon''_\perp = \varepsilon_{\perp\infty} + \frac{\Delta\varepsilon_\perp}{(1 + i\frac{f}{f_R})^\beta} + \frac{\sigma}{i2\pi f\varepsilon_0}$$

DISCUSSION OF EXPERIMENTAL RESULTS

Below 1 MHz frequency for studied compounds and mixtures only one relaxation process was detected in all studied phases. The temperature dependences of parameters $\Delta\varepsilon$, $\Delta\varepsilon^{-1}$ and f_R obtained from fitting are presented in Figures 1, 2, 3 and 4. The phase transitions can be clearly detected from these characteristics. It is well known [4–6] that the phase transition SmC$_\alpha$* $\Rightarrow$ SmA is clearly detected due to a change in the slope of the linear temperature dependences of relaxation frequency f_R and inverse dielectric strength $\Delta\varepsilon^{-1}$. From our experimental results (see Figs. 1 and 2) the phase transition temperatures SmC$_\alpha$* $\Rightarrow$ SmA were determined for compound 2 – 120.0°C and for mixture 1:2(0.90) – 126.3°C. In the SmA phase the relaxation frequency linearly depends on temperature with slope 21.17 kHz/°C for compound 2 and 24.88 kHz/°C for mixture 1:2(0.90). But in the SmC$_\alpha$* phase these slopes are 1.82 kHz/°C and 3.09 kHz/°C, respectively. The temperature at which the phase transition SmC* $\Rightarrow$ SmC$_\alpha$* occurs is assumed to be 118.4°C for compound 2 and 125°C for mixture 1:2(0.90). In SmC* phases observed relaxation processes are typical Goldstone mode with high dielectric strength and low relaxation frequencies ($f_R < 10$ kHz), which slightly depend on temperature.

For compound 1 and mixture 1:2(0.15) discontinuity of the temperature dependences of dielectric strength and relaxation frequency are observed at 150.4°C and at 147.0°C, respectively (see Figs. 3 and 4). We assumed these temperatures as the phase transition temperatures SmC* $\Rightarrow$ SmA, they are in good agreement with temperatures detected from DSC measurements [3].

It was shown by V. Bourny *et al.* in [6], that the phase transition SmC* $\Rightarrow$ SmC$_\alpha$* is characterized by a strong maximum for low frequencies and a minimum for high frequencies of temperature dependence of real

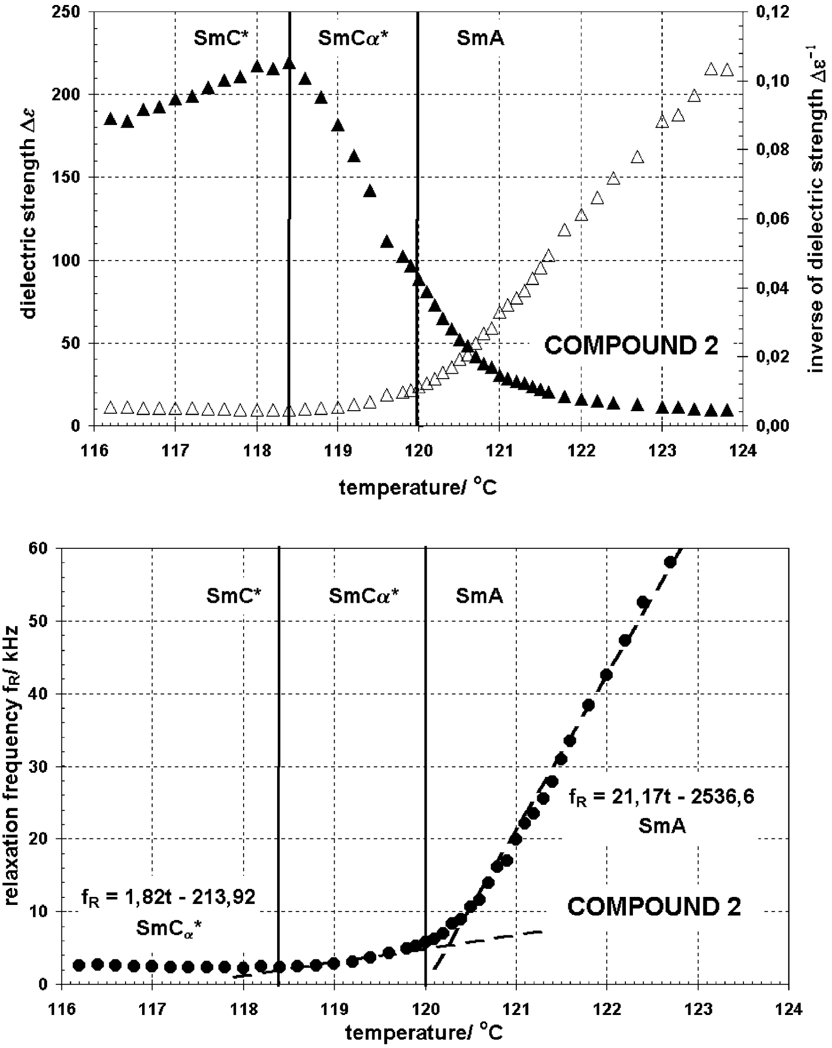


FIGURE 1 Temperature dependences of dielectric strength, inverse of dielectric strength and relaxation frequency for compound 2.

part of dielectric permittivity. In accordance with this rule, from our experimental results (see Figs. 5A and 5B) the phase transition temperatures $SmC^* \Rightarrow SmC_\alpha^*$ were determined for compound 2 – 118.4°C and mixture 1:2(0.90) – 125.0°C. One can see good conformity with temperatures obtained from temperatures dependences of relaxation frequency and inverse of dielectric strength.

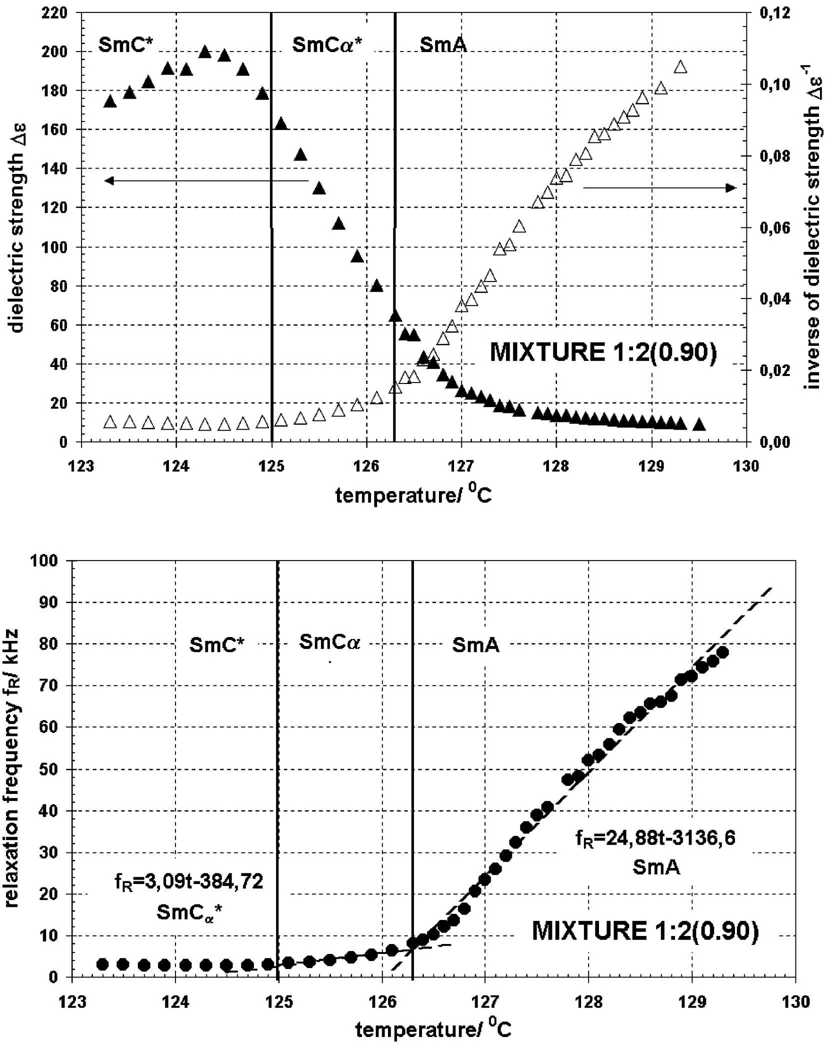


FIGURE 2 Temperature dependences of dielectric strength, inverse of dielectric strength and relaxation frequency for mixture 1:2(0.90).

Temperature ranges of SmC$_\alpha$* phase existence for compound 2 and mixture 1:2(0.90) found by dielectric measurements are rather narrow near (1°C) and they differ insignificantly from those determined by DSC [3]. But because of the strong electroclinic effect and fluctuation of the angle in the SmA phase near the phase transition to SmC$_\alpha$*, the phase transition temperature is difficult to establish exactly by dielectric measurements.

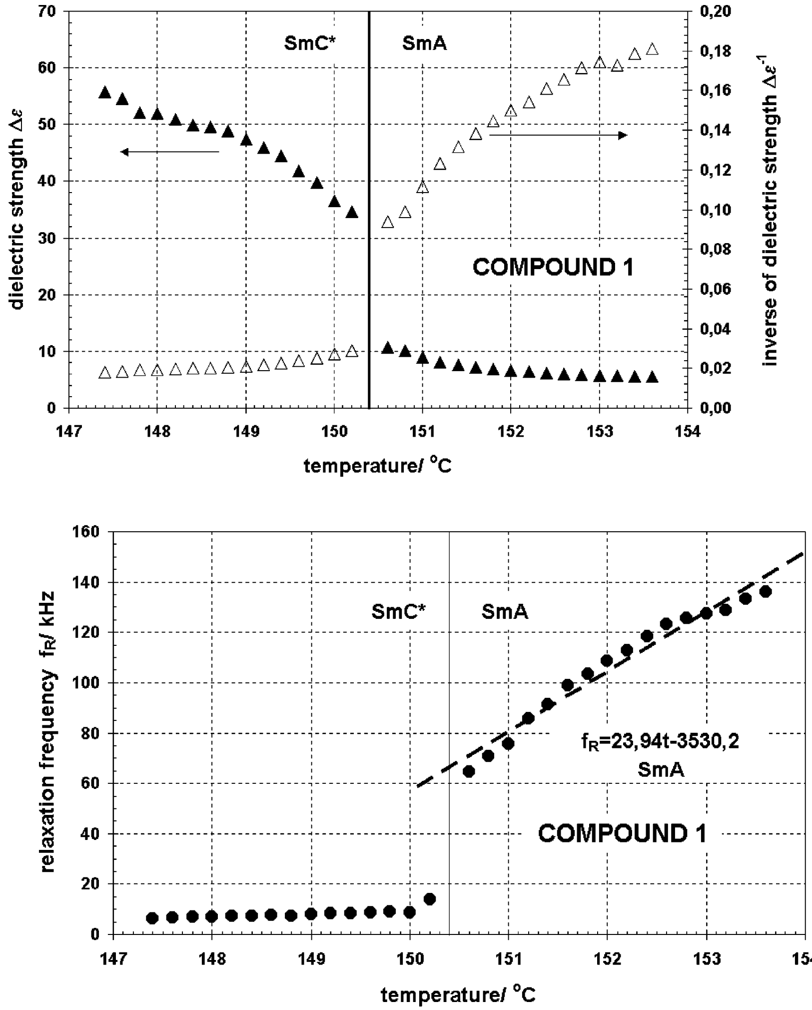


FIGURE 3 Temperature dependences of dielectric strength, inverse of dielectric strength and relaxation frequency for compound 1.

To have a better understanding of the origin of the relaxation process observed in the SmC_{α}^{*} phase we have performed dielectric measurements under the DC bias field. The temperature dependences of parameters $\Delta\varepsilon$, $\Delta\varepsilon^{-1}$ and f_R obtained from fitting to Cole-Cole equation for different bias field are displayed in Figures 6 and 7 for compound 2 and mixture 1:2(0.90), respectively. Our results are similar to these published earlier in [4,5,7].

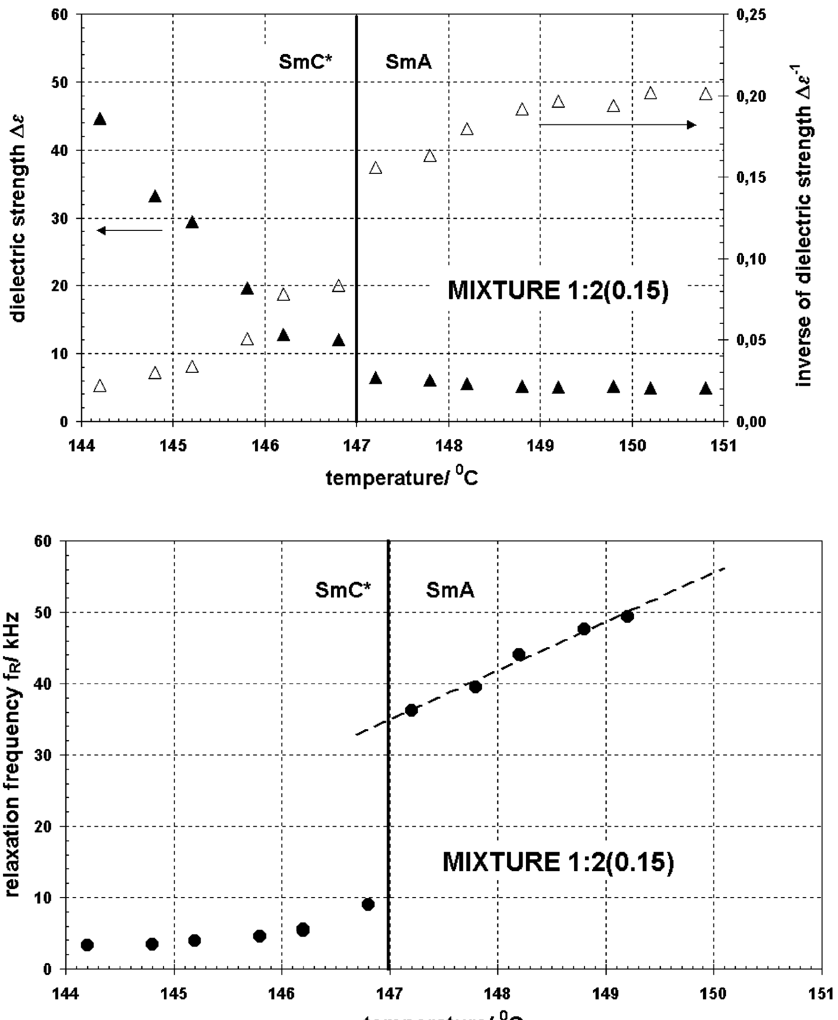


FIGURE 4 Temperature dependences of dielectric strength, inverse of dielectric strength and relaxation frequency for mixture 1:2(0.15).

Dielectric behaviour detected in SmA and SmC* phases in both compound 2 and mixture 1:2(0.90) are connected respectively with the soft mode and Goldstone mode. The relaxation frequency f_R and inverse dielectric strength $\Delta\varepsilon^{-1}$ linearly depend on temperature and under bias field weak variations of them are observed.

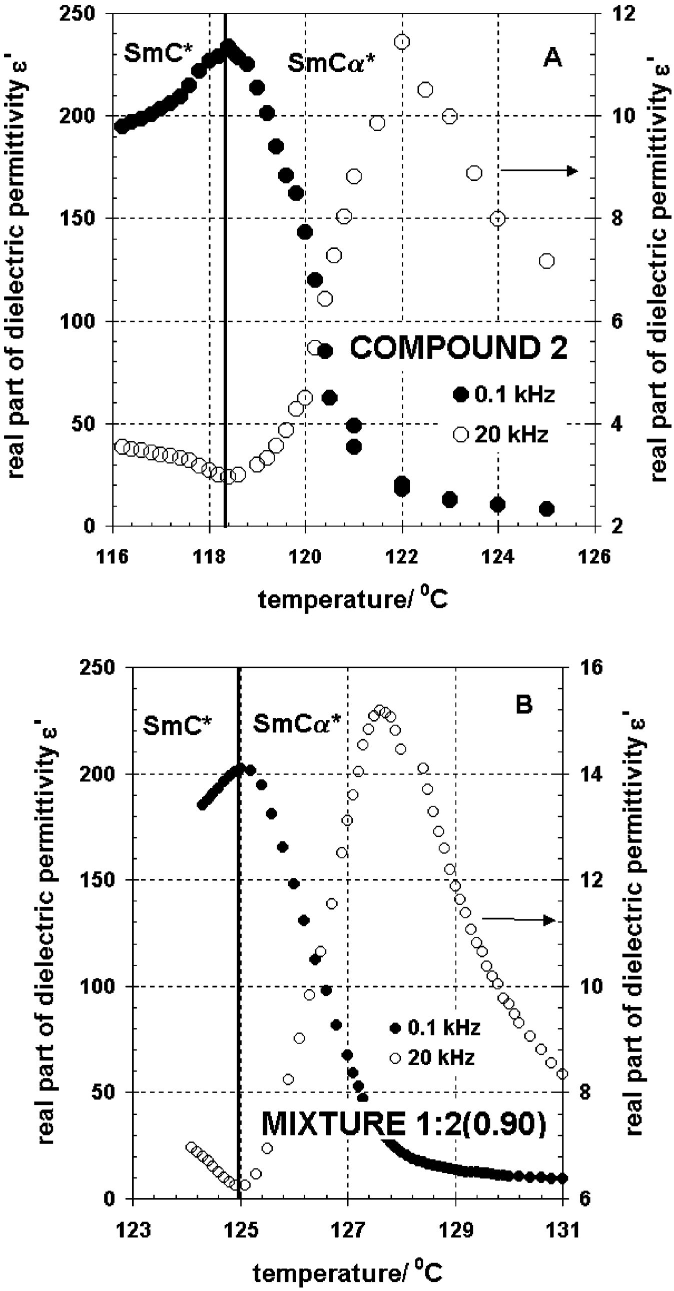
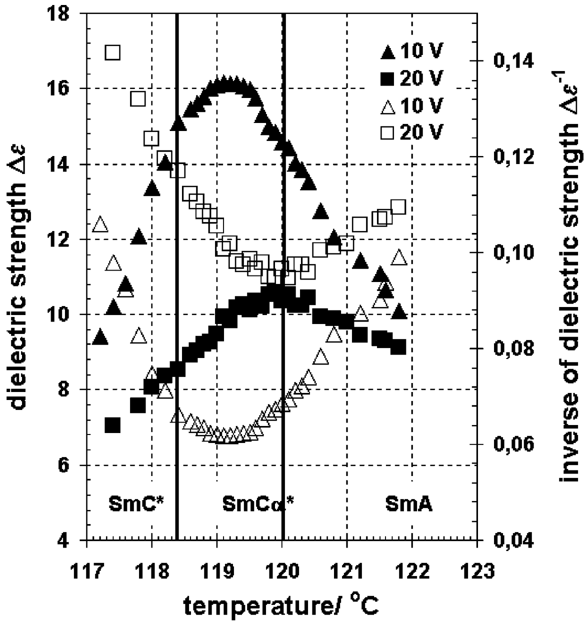


FIGURE 5 The temperature dependence of the dielectric permittivitty at the frequency 0.1 kHz and 20 kHz for A – compound 2 and B – mixture 1:2(0.90).



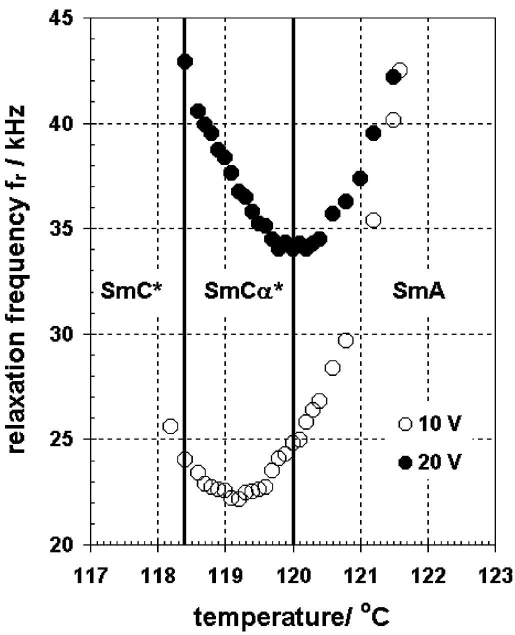


FIGURE 6 Temperature dependences of dielectric strength, inverse of dielectric strength and relaxation frequency for compound 2 with different DC bias.

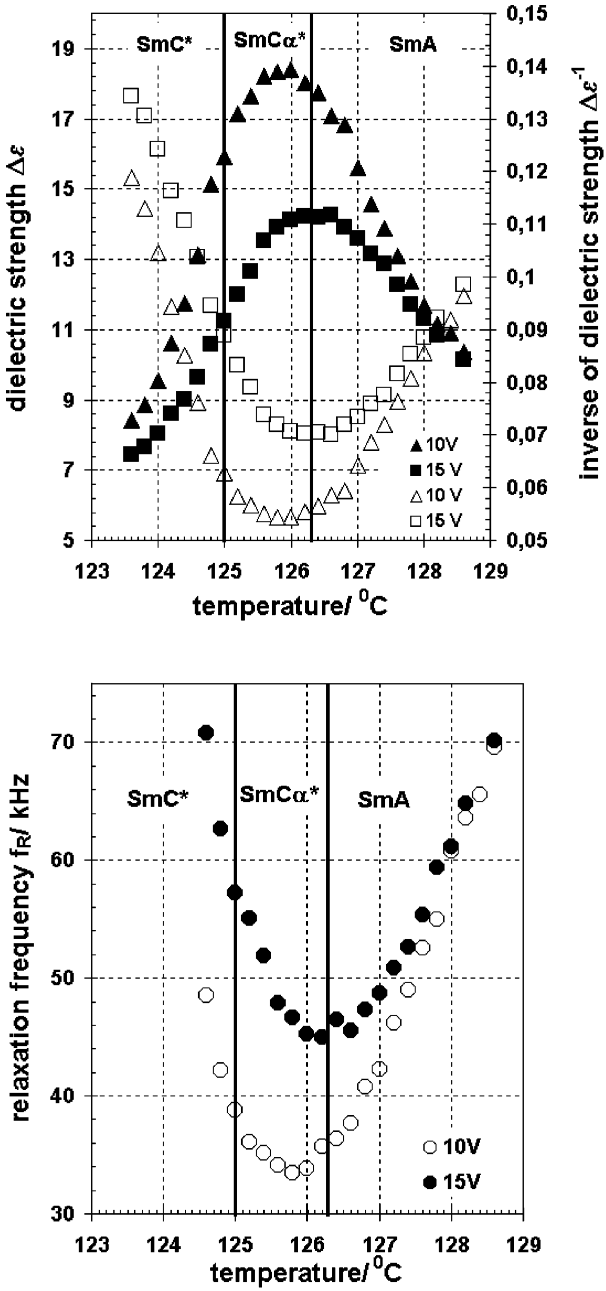


FIGURE 7 Temperature dependences of dielectric strength, inverse of dielectric strength and relaxation frequency for mixture 1:2(0.90) with different DC bias.

Under bias field the helicoidal structure in SmC* starts to unwind and Goldstone mode begins to be suppressed, so bias field causes the dielectric strength $\Delta\varepsilon$ to decrease and relaxation frequency f_R to increase.

In the SmC$_\alpha$* phase for compound 2 and mixture 1:2(0.90) the relaxation process is strongly modified under bias field. The relaxation process shifts at high frequency and its dielectric strength is strongly lowered (see Figs. 6 and 7). The dielectric strength $\Delta\varepsilon$ and relaxation frequency f_R are respectively maximum and minimum at the SmA ⇒ SmC$_\alpha$* phase transition.

At enough high bias at 20 V for compound 2 and 14 V for mixture 1:2(0.90) linear temperature dependence of the relaxation frequency f_R and inverse dielectric strength $\Delta\varepsilon^{-1}$ are observed from one part to the other of SmA ⇒ SmC$_\alpha$* phase transition. So relaxation process observed in the SmC$_\alpha$* at high bias presents a soft mode behaviour.

CONCLUSIONS

Our experimental results lead to conclusion that precise but simple dielectric measurements seemed to be an effective experimental method to determining the phase transition SmC$_\alpha$* ⇒ SmA and SmC* ⇒ SmA.

At high bias field behaviour the relaxation process observed in the SmC$_\alpha$* in the function of temperature is characteristic of the soft mode at the SmC* ⇒ SmA phase transition, usually observed under bias field. These show that SmC$_\alpha$* phase in the studied non-fluorinated esters: compound 2 and mixture 1:2(0.90) composed of 0.9 mole fraction of compound 2 has a simple helical structure and is similar to the SmC* phase. As the helicoidal structure is unwound and soft mode behaviour on the both sides of SmA ⇒ SmC$_\alpha$* is observed. This relaxation process is probably connected with the helicity of SmC$_\alpha$* phase e.g. ferroelectric-like structure of this phase.

REFERENCES

[1] Rutkowska, J., Perkowski, P., Kędzierski, J., Raszewski, Z., Dąbrowski, R., Gauza, S., Czupryński, K., & Miszczyk, E. (2000). Physical properties of components of mixture with induced SmC$_A$* phase. In: *Liquid Crystals: Chemistry, Physics and Applications*, Kłosowicz, S., Rutkowska, J., Zieliński, J., & Żmija, J. (Eds.), Proceedings of SPIE, 4147, 101–108.

[2] Rutkowska, J., Kędzierski, J., Raszewski, Z., Perkowski, P., Dąbrowski, R., Gauza, S., & Czupryński, K. (2001). Properties of system with induced SmC$_A$* phase. *Mol. Cryst. Liq. Cryst.*, *366*, 617–628.

[3] Gauza, S., Czupryński, K., Dąbrowski, R., Kuczyński, W., & Pociecha, D. (2001). Bicomponent system with induced antiferroelectric SmC$_A$* phase. *Mol.Cryst. Liq.Cryst.*, *365*, 189–198.

[4] Douali, R., Legrand, C., & Nguyen, H T. (2000). Temperature dependence of $S_{C\alpha}{}^*$ phase electric field behaviour as evidenced by polarization current and dielectric measurements. *Ferroelectric.*, *245*, 101–110.
[5] Douali, R., Legrand, C., Faye, V., & Nguyen, HT. (1999) Dielectric dispersion in the $S_{C\alpha}{}^*$ phase of an antiferroelectric liquid crystal. *Mol. Cryst. Liq. Cryst.*, *328*, 209–219.
[6] Bourny, V., Pavel, J., Lorman, V., & Nguyen, H T. (2000). Phase transitions in the antiferroelectric liquid crystal C8 tolane determined by dielectric and electro-optical measurements. *Liq. Cryst.*, *27*, 559– 566.
[7] Sarmento, S., Carvalho, P., Chaves, M., Nguyen, H T., & Pinto, F. (1999). Ferroelectric-like and antiferroelectric-like behaviour of the $SmC_\alpha{}^*$ phase. *Mol. Cryst. Liq. Cryst.*, *328*, 457–465.