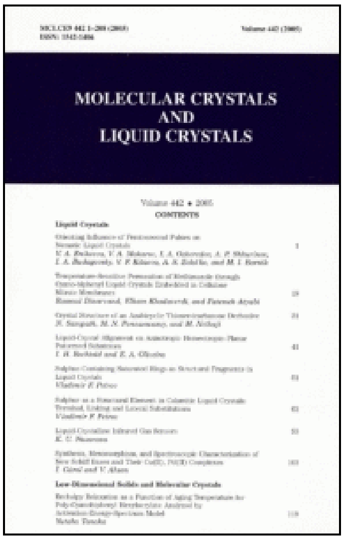


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

High Frequency Mode in New Antiferroelectric Mixture

P. Perkowski[a]; K. Ogrodnik[a]; W. Piecek[a]; Z. Raszewski[a]; M. Żurowska[b]; R. Dąbrowski[b]
[a] Institute of Applied Physics, Military University of Technology, Warsaw, Poland [b] Institute of Chemistry, Military University of Technology, Warsaw, Poland

First published on: 13 July 2010

To cite this Article Perkowski, P. , Ogrodnik, K. , Piecek, W. , Raszewski, Z. , Żurowska, M. and Dąbrowski, R.(2010) 'High Frequency Mode in New Antiferroelectric Mixture', Molecular Crystals and Liquid Crystals, 525: 1, 50 — 56

To link to this Article: DOI: 10.1080/15421401003795969

URL: http://dx.doi.org/10.1080/15421401003795969

Mol. Cryst. Liq. Cryst., Vol. 525: pp. 50–56, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421401003795969

Taylor & Francis
Taylor & Francis Group

High Frequency Mode in New Antiferroelectric Mixture

P. PERKOWSKI,[1] K. OGRODNIK,[1] W. PIECEK,[1]
Z. RASZEWSKI,[1] M. ŻUROWSKA,[2] AND
R. DĄBROWSKI[2]

[1]Institute of Applied Physics, Military University of Technology,
Warsaw, Poland
[2]Institute of Chemistry, Military University of Technology,
Warsaw, Poland

New antiferroelectric fluorinated mixture W-1000 was made. Typical two dielectric modes with frequencies around 1–10 kHz and 100 kHz–1 MHz were detected in SmC_A^*. *Additionally high frequency mode was observed with relaxation frequency higher than 1 MHz. All modes in antiferroelectric phase were discussed.*

Keywords Antiferroelectric liquid crystal; dielectric modes; relaxation frequency

Introduction

Dielectric spectroscopy measurement is a very important and useful experimental technique for characterisation of liquid crystal phases. In smectic liquid crystals phases many dielectric modes are detected (Soft, Goldstone, P_H, P_L modes) [1,2].

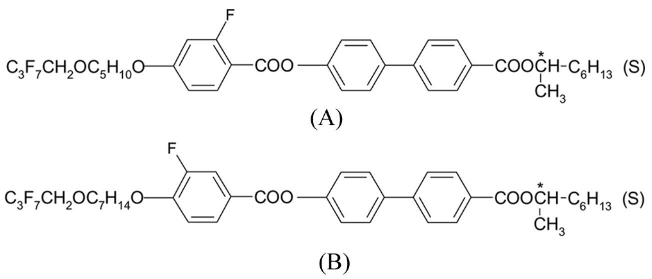
New antiferroelectric mixture W-1000, prepared in Military University of Technology was studied by dielectric means. Apart from typical relaxations detected in smectics, the high frequency relaxation was found. Such high frequency relaxation was firstly announced in pure fluorinated antiferroelectric compound [3]. The activation energy for all modes in SmC_A^* were calculated and behavior of these modes were discussed.

Investigated Mixture

Two components, earlier investigated [3], compose the mixture W-1000. Component A gives 0.52519 weight %, while B-component gives 0.47481 weight %. Three smectic phases were found with the following temperatures of phases transitions (obtained from DSC):

$$\mathrm{Cr} < 10^\circ\mathrm{C}\ \mathrm{SmC}_A^*\ 101^\circ\mathrm{C}\ \mathrm{SmC}^*\ 103.5^\circ\mathrm{C}\ \mathrm{SmA}^*\ 105.9^\circ\mathrm{C}\ \mathrm{Iso}.$$

Address correspondence to P. Perkowski, Institute of Applied Physics, Military University of Technology, Warsaw, Poland. Tel.: +48 22 683 95 79; E-mail: pperkowski@wat.edu.pl



(A)

(B)

Figure 1. Molecular structure of both components.

In measuring cell the temperatures were a little higher but the phase sequence was not changed. This mixture shows, as far as authors know, one of the broadest, very stable antiferroelectric smectic phase.

Experimental Setup

Hewlet Packard impedance analyser HP 4192A was used for dielectric spectroscopy. The measuring AC field was 0.1 V. Cell with golden electrodes were prepared in our laboratory. Cell thickness d was 5.2 mm. Frequencies of measuring field were from 100 Hz up to 10 MHz. The BIAS DC voltage changed from 0 V up to 15 V.

To find parameters of Cole-Cole model special software (COLE-COLE.VEE) created in our laboratory was applied. It allows us to calculate relaxation frequency f_R, dielectric strength $\Delta\varepsilon$, static electric permittivity ε_S and optical limit of electric permittivity ε_∞.

To make possible the measurements with temperature, Linkam TMS 92 controller and THMSE 600 hot-stage were applied.

Experimental Results

In the Figure 2 the real part (ε') of electric permittivity, while in the Figure 3 the imaginary part of electric permittivity (ε'') are presented as a function of temperature. One can see that SmA* phase is narrow (2–3°C). SmC* is a little bit broader (6–7°C). And SmC_A^* is very wide, stable phase (temperature of crystallization is below the room temperature). One can notice that the shapes of (ε'') for different frequencies suggest that relaxation frequencies change a lot in antiferroelectric phase and that it should be more than one mode in SmC_A^*. Two relaxation modes were earlier detected in SmC_A^* (anti-phase azimuthal angle fluctuations, so called P_H [1] or the antiferroelectric Goldstone mode [5] and in phase azimuthal angle fluctuations, so called P_L mode [1] or helical Goldstone mode [6]). High value of (ε'') for low temperatures and for frequency 1 MHz suggests that it can be caused by extra relaxation (with relaxation frequency higher than 1 MHz). Because such high frequency relaxation was found in another fluorinated AFLC [3] we decided to investigated it more detailed in this mixture. In our previous work we called this mode: X-mode [3]. What is worth to underline, the studied mixture possesses the broad antiferroelectric phase and it is easy to study the temperature dependence of relaxation frequencies in SmC_A^* and check if modes fulfill the Arrhenius law.

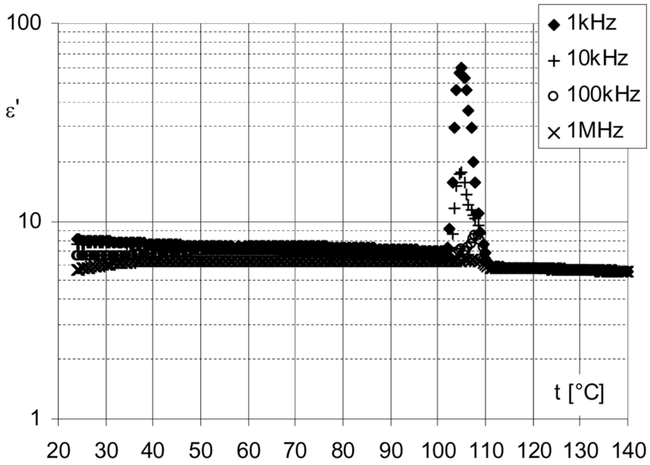


Figure 2. Real part of electric permittivity (ε') for four frequencies (1 kHz, 10 kHz, 100 kHz, 1 MHz) as a function of temperature.

In the Figure 4 relaxation frequencies found for all detected modes in W-1000 are shown. It is worth to underline, that when the temperature decreases, X-mode starts to be detected, when P_L mode is not seen any more. The P_H-mode is detectable for the whole temperature range of SmC_A^* phase. Soft mode frequency depends on temperature. Goldstone mode is constant with the temperature. Frequencies of all three modes in antiferroelectric decrease when the temperature is decreasing. All three modes are well separated in frequency domain. Between P_L and P_H there is 1–2 decades frequency gap as well as between X-mode and P_H.

In the Figure 5 the dielectric strength is shown. One can see that dielectric strength of soft mode and Goldstone mode depend on temperature strongly, while for P_L, P_H and X-mode temperature dependence is rather weak. Only for X-mode

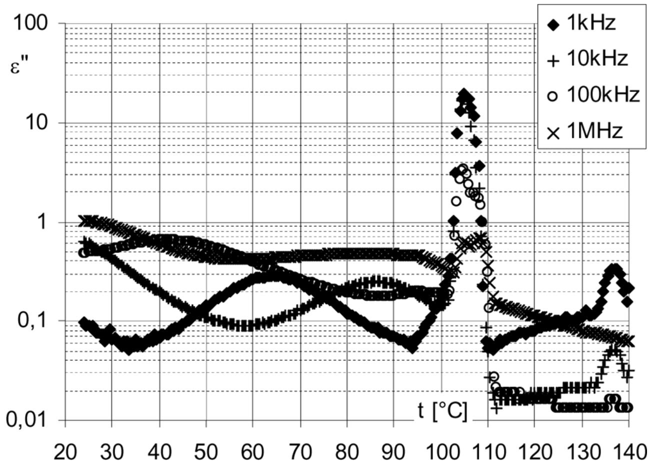


Figure 3. Imaginary part of electric permittivity (ε'') for four frequencies (1 kHz, 10 kHz, 100 kHz, 1 MHz) as a function of temperature.

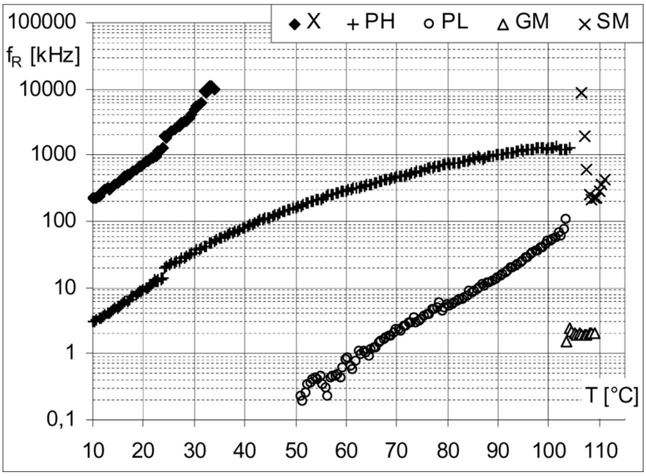


Figure 4. Relaxation frequencies for all detected modes (SM – soft mode, GM – Goldstone mode, PL – P_L mode, PH – P_H mode, X – high frequency mode in SmC_A^*) in logarithmic scale.

close to temperature, when it appears the temperature dependence of dielectric strength of X-mode is more distinct.

In the Figure 6 the Arrhenius plots for all modes in antiferroelectric phase are presented. Because the temperature range of mode existing is rather broad then Arrhenius plots are not exactly line but they are close to straight lines. So we decided to find the activation energies for some parts of these plots. From slope of the plots 6 we found activation energies shown in Table 1. Beyond all doubt activation energy of P_H ($0.387 \div 0.830$ eV) is lower than activation energy P_L mode (1.089 eV). This rule was found in other papers [7,8]. Activation energy for P_H in lower temperatures (0.830 eV) is higher than for higher temperatures (0.387 eV). The opposite effect is

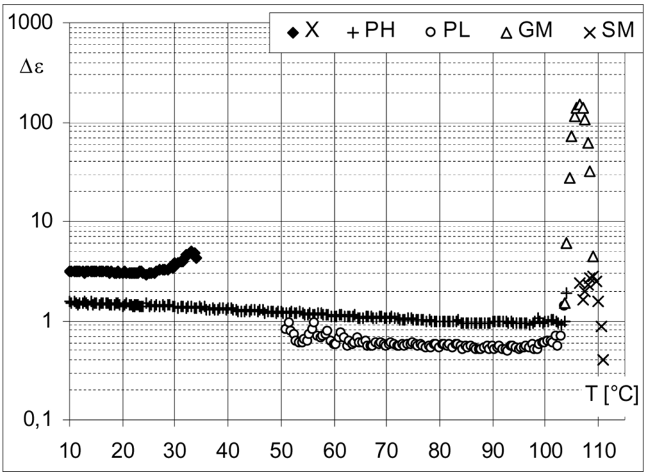


Figure 5. Dielectric strength Δε of all detected modes (SM – soft mode, GM – Goldstone mode, PL – P_L mode, PH – P_H mode, X – high frequency mode in SmC_A^*) in logarithmic scale.

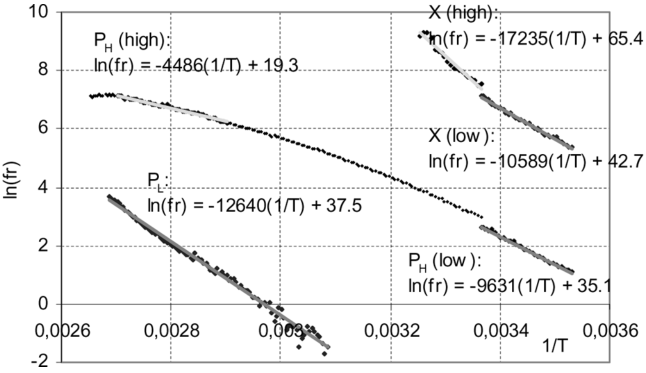


Figure 6. Arrhenius plots for all modes (P_L, P_H and X-mode) detected in SmC_A^*.

Table 1. Activation energies calculated from Arrhenius plots for all dielectric modes found in SmC_A^* phase

	P_L	P_H (high)	P_H (low)	X (high)	X (low)
E_A [eV/molecule]	1.089	0.387	0.830	1.485	0.912

noticeable for X-mode. For higher temperatures activation energy of X-mode is higher (1.485 eV) than for lower temperatures (0.912 eV). Is seems that mechanism (molecular or collective) of X-mode is easier to do when the SmC_A^* phase comes close to crystalline phase. It is worth to stress that activation energy for X-mode is higher than for P_H and P_L modes.

In the Figure 7–9 Cole-Cole plots for SmC_A^* are presented for three temperatures: 85°C (when P_L and P_H are detected), 40°C (when P_H only appears) and 25°C (when both: P_H and X-mode exist). Dielectric strength of both modes: P_H and P_L modes increase with increasing the BIAS voltage, while X-mode is weaker

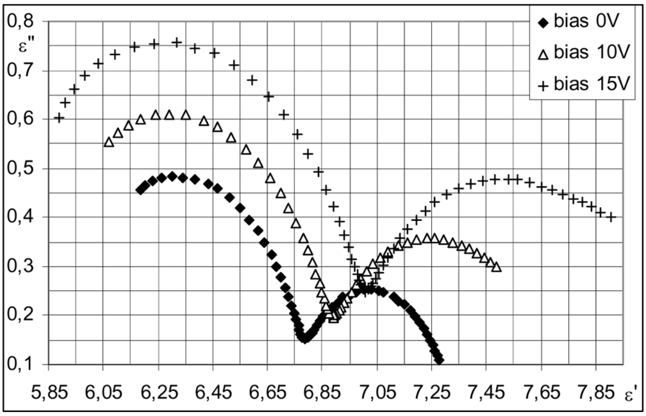


Figure 7. Cole-Cole plots in SmC_A^* phase for temperature when P_L and P_H mode exist (85°C). When BIAS electric field increases dielectric strength of both modes increase as well.

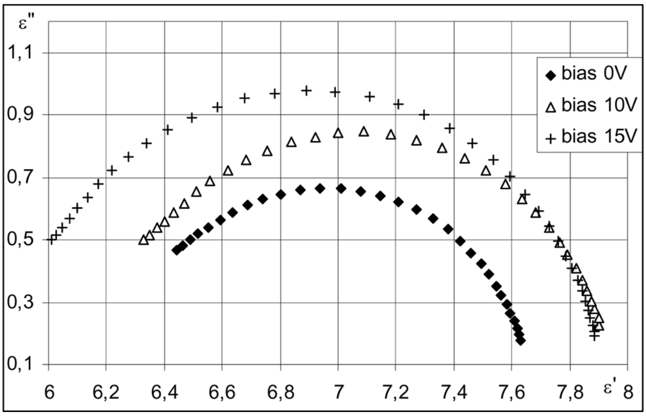


Figure 8. Cole-Cole plots in SmC$^*_A$ phase for temperature when P_H mode exist (40°C). When BIAS electric field increases dielectric strength of P_H mode increases as well.

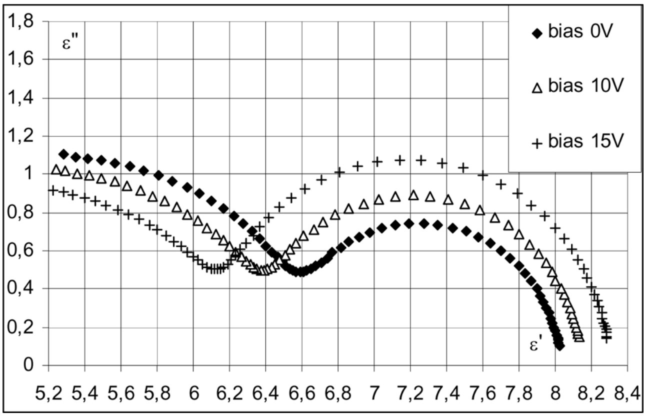


Figure 9. Cole-Cole plots in SmC$^*_A$ phase for temperature when both P_H and X modes exist (25°C). When BIAS electric field increases dielectric strength of P_H mode increases, while dielectric strength of X-mode decreases.

when DC field is applied. All modes are slower slightly with the BIAS field than without DC voltage.

Conclusions

Investigated mixture W-1000 possesses a very broad antiferroelectric phase. Owing to such broad phase it is possible to observe the temperature behavior of all modes in SmC$^*_A$. It helps to make Arrhenius plots. Before it was impossible because we had just a few temperature points of X-mode [3]. Detected frequency of X-mode is 1–2 decades higher than P_H mode, while P_H is 1–2 decades faster than P_L mode. X-mode is weaker when the DC voltage is applied, while P_L and P_H modes are stronger with BIAS field.

The question arises why this mode is detected rather seldom? It seems that reason was the quality of measuring cells. When we used ITO cells it was not possible to measure dielectric properties for frequencies higher than 100 kHz practically [9]. When the theory was coined [10], numerical procedures and new golden measuring cells the limit was shifted almost to 5 MHz and it allows to observe the relaxation modes for higher frequencies than before. It seems that this mode can be the earlier predicted antiferroelectric soft mode [4,6] which was believed to be able for dielectric spectroscopy detection.

The important evidence that this mode is not related to measuring cell property (cut-off frequency) is that high frequency limit of electric permittivity (ε_∞) for this mode is around 2–4. In case this mode had its source in cell property ε_∞ would be less than one [10].

References

[1] Buivydas, M., Gouda, F., Andersson, G., Lagerwall, S. T., Stebler, B., Bömelburg, J., Heppke, G., & Gestblom, B. (1997). *Liquid Crystals*, *23*(5), 723.

[2] Haase, W. & Wróbel, S. (2003). *Relaxation Phenomena*, Springer: Berlin, Germany.

[3] Perkowski, P., Piecek, W., Raszewski, Z., Ogrodnik, K., Rutkowska, J., Żurowska, M., Dąbrowski, R., Kędzierski, J., & Sun, X. (2008). *Ferroelectrics*, *365*, 88.

[4] Pandey, M. B., Dabrowski, R., & Dhar, R. (2007). *Physica B*, *387*, 25.

[5] Hiraoka, K., Takezoe, H., & Fukuda, A. (1993). *Ferroelectrics*, *147*, 13.

[6] Hiraoka, K., Taguchi, A., Ouchi, Y., Takezoe, H., & Fukuda, A. (1990). *Jpn. J. Appl. Phys.*, *29*, L103.

[7] Mikułko, A., Douali, R., Legrand, Ch., Marzec, M., Wróbel, S., & Dąbrowski, R. (2005). *Phase Transitions*, *78*(12), 949.

[8] Bhattacharyya, S. S., Rahman, M., Mukherjee, A., Wu, S. L., & Chaudhuri, B. K. (2009). *Current Applied Physics*, *9*, 390.

[9] Perkowski, P., Łada, D., Ogrodnik, K., Rutkowska, J., Piecek, W., & Raszewski, Z. (2008). *Opto-electronics Review*, *16*(3), 271.

[10] Perkowski, P. (2009). *Opto-electronics Review*, *17*(2), 180.