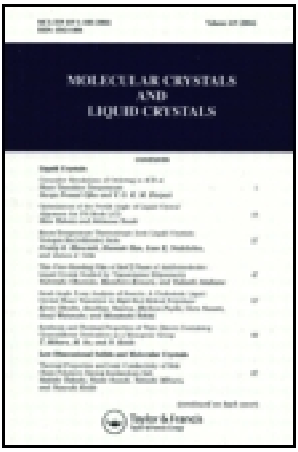

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Dielectric Measurements of Orthoconic Antiferroelectric Liquid Crystal Mixtures

K. Ogrodnik [a] , P. Perkowski [a] , Z. Raszewski [a] , W. Piecek [a] , M. Żurowska [b] , R. Dąbrowski [b] & L. Jaroszewicz [a]

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

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

Version of record first published: 16 Jun 2011

To cite this article: K. Ogrodnik, P. Perkowski, Z. Raszewski, W. Piecek, M. Żurowska, R. Dąbrowski & L. Jaroszewicz (2011): Dielectric Measurements of Orthoconic Antiferroelectric Liquid Crystal Mixtures, Molecular Crystals and Liquid Crystals, 547:1, 54/[1744]-64/[1754]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.572515

Mol. Cryst. Liq. Cryst., Vol. 547: pp. 54/[1744]–64/[1754], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.572515

Dielectric Measurements of Orthoconic Antiferroelectric Liquid Crystal Mixtures

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

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

Three new antiferroelectric mixtures W-1000, W-1000A and W-1000B and their components W-1, W-2 and B-3 synthesized at Military University of Technology were investigated by dielectric spectroscopy. Typical relaxation modes in smectic phases and one mode in isotropic phase never observed before were detected. Obtained results were discussed in terms of composition of investigated mixtures and molecular structures of their components.

Keywords Antiferroelectric liquid crystal; dielectric modes; relaxation frequency

1. Introduction

A binary mixture W-1000 exhibiting very broad orthoconic antiferroelectric smectic phase (OAFLC) was recently prepared [1] and studied [2]. Extensive investigations proved the excellent electrooptical performance of this mixture, characterized by extraordinary optical contrast and light-leakage free optical switching. This attractive properties are easily achievable due to the perfect optical uniformity of the surface stabilized, quasi-bookshelf structure and the helical pitch as long as 4.7 μm. Such a helical pitch is longer than the typical cell gap [3]. However, the switching time of this mixture is too long for successful application of this mixture [1]. Therefore, the dynamic properties and molecular movement were investigated. As to test the influence of a homostructural, racemic dopant with different value and orientation of the molecular dipole moment on the physical and dielectric parameters of the parent W-1000 mixture a two additional mixtures W-1000A and W-1000B were formulated. Antiferroelectric mixtures W-1000 and two doped mixtures W-1000A and W-1000B were investigated by dielectric spectroscopy.

The obtained results were discused in terms of composition of investigated mixtures as well as molecular structures and chirality of their components.

Address correspondence to K. Ogrodnik, Institute of Applied Physics, Military University of Technology, 00-908 Warsaw, Poland. Tel.: +48 22 683 70 66; E-mail: kogrodnik@wat.edu.pl

W-1

W-2

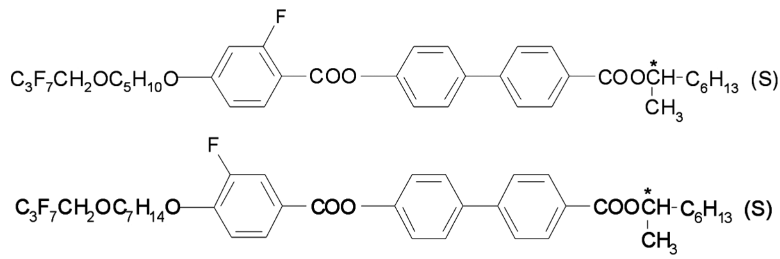

Figure 1. Molecular structures of components W-1 and W-2 of W-1000 mixture.

A-3

B-3

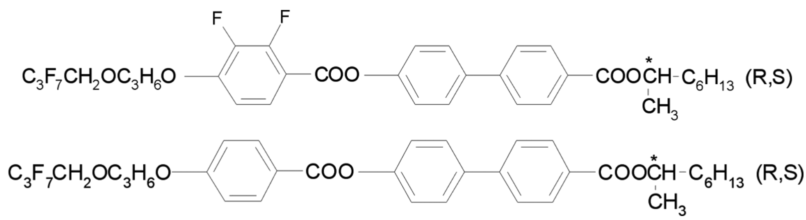

Figure 2. Molecular structures of dopants A-3 and B-3 in W-1000A and W-1000B mixtures respectively.

2. Investigated Materials

The parent, bi-component, near equimolar mixture, W-1000 consists of two components: chiral compounds: W-1 (S) (52.519 weight %) and W-2 (S) (47.481 weight%) (see Fig. 1).

Two doped mixtures W-1000A and W-1000B were prepared by doping of the W-1000 mixture with homostructural, racemic compounds: A-3 (R,S) and B-3 (R,S) respectively. There are two main differences between all four homologous components of W-1000, W-1000A and W-1000B mixtures (see Fig. 1 and Fig. 2); one is the position of the fluorine atom substituted at the phenyl ring within the molecular rigid core, the other is a number of CH_2 alkoxy groups (within protonated spacer) at the terminal chain. Isomeric components W-1 (S) and W-2 (S) doped with racemic ones A-3 (R,S) and B-3 (R,S) lead to a long helical pitch mixture. Their synthesis and electrodynamic characterization is given in references [4–7].

In mixtures W-1000A and W-1000B dopants A-3 and B-3 are taken as an eutectic composition. Accordingly in mixture W-1000A component W-1 gives 33.938 weight %, component W-2 gives 34.568 weight % and component A-3 gives 31.494 weight %.

Three smectic phases were recognised for all studied mixtures W-1000, W-1000A and W-1000B. Their mesogenic behaviour was studied by DSC method and the results are collected in the Table 1.

3. Experiment

The dielectric spectroscopy studies of OAFLC mixtures were done using HP 4192A Hewlett Packard impedance analyser. Temperature of samples was controlled with

Table 1. Temperatures T [°C] and enthalpies ΔH [J/g] of phase transition obtained from DSC for investigated mixtures

W-1000	SmC^*_A	99.8	SmC^*	101.3	SmA^*	103.3	Iso	T[°C]
		0.11		*1.19*		*4.8*		*ΔH [J/g]*
W-1000A	SmC^*_A	96.9	SmC^*	98.5	SmA^*	100.5	Iso	T[°C]
		0.1		*1.26*		*5.3*		*ΔH [J/g]*
W-1000B	SmC^*_A	100.3	SmC^*	102.8	SmA^*	104.8	Iso	T[°C]
		0.08		*1.31*		*5.1*		*ΔH [J/g]*

Linkam THMSE 600 hot stage with accuracy of 0.1°C. The measuring AC voltage used during experiment was U = 0.1 V and at frequencies from 100 Hz up to 1 MHz. For the dielectric investigations a couple of custom made cells were used. The proper measuring conditions were assured by using of golden electrodes evaporated on the inner surface of cells. The uniform homogeneous alignment of OAFLCs within cells was induced by using of the PI 2610 polyimide layer spincoated on electrodes. The thicknesses *d* of measuring cells was fixed by deposition of glass spacer of diameter 5 [μm] on the cell surface before cell assembling. The wiring was soldered to the electrodes by using of the ultrasonic soldering unit and a proper, custom made alloy. Before the filling with studied OAFLC, each cell was examined and two parameters were evaluated; C_0 – capacity of the empty cell and C_M – the montage capacity (which is regarded to be constant for all measurements done).

Cells were filled with mixtures under study by the capillary action at the temperature above the temperature of isotropization. Next, cells were slowly cooled (with the cooling rate of 0.2°C/min) as to obtain a surface stabilised bookshelf-like structure. The measurements were done every half of a degree upon cooling cycle, starting from the temperature close to the temperature of isotropization to the room temperature. The temperature and frequency dependence of the cell capacity was automatically collected and subsequently analysed by using of the custom made software.

4. Results and Discussion

One can see (Fig. 3) that SmA^* phase is narrow (2–3 degree), SmC^* phase is a little bit broader (6–7 degree) and SmC^*_A is a very broad and stable phase. The shapes of

Table 2. Temperatures T [°C] and enthalpies ΔH [kJ/mol] of phase transition obtained from DSC for investigated components

W-1 (S)	Cr	28.1	SmC^*_A	97.0	SmC^*	–	SmA^*	99.0	Iso	T[°C]
		34.9		*0.1*		–		*5.4*		*ΔH [kJ/mol]*
W-2 (S)	Cr	37.4	SmC^*_A	103.1	SmC^*	104.3	SmA^*	109.1	Iso	T[°C]
		25.6		*0.065*		*0.77*		*3.8*		*ΔH [kJ/mol]*
A-3 (R,S)		48.3	SmC^*_A	95.6	SmC^*		98.1		Iso	T[°C]
		20.3		*0.041*			*5.2*			*ΔH [kJ/mol]*
B-3 (R,S)		70.3	SmC^*_A	110.0	SmC^*	–	111.5		Iso	T[°C]
		19.5		*0.54*		–	*2.4*			*ΔH [kJ/mol]*

–it is not seem by DSC.

Table 3. The parameters of empty measuring cells used for studies

Cell param.	W-1000	W-1 000A	W-1000B	W-l	W-2
d [μm]	5.2	5.1	5.4	5.4	5.0
C_0 [pF]	59.3	58.4	55.0	57.5	57.1
C_M [pFl	0.4	0.3	2.4	0.9	0.8

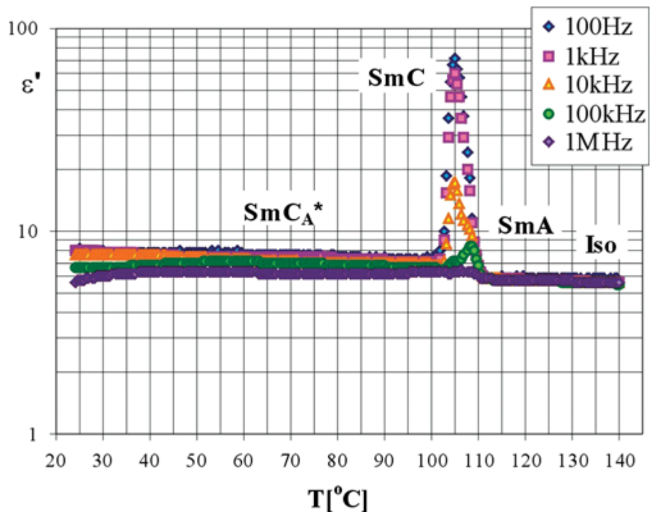

Figure 3. Real part ε' of the electric permittivity of W-1000 mixture as a function of the temperature.

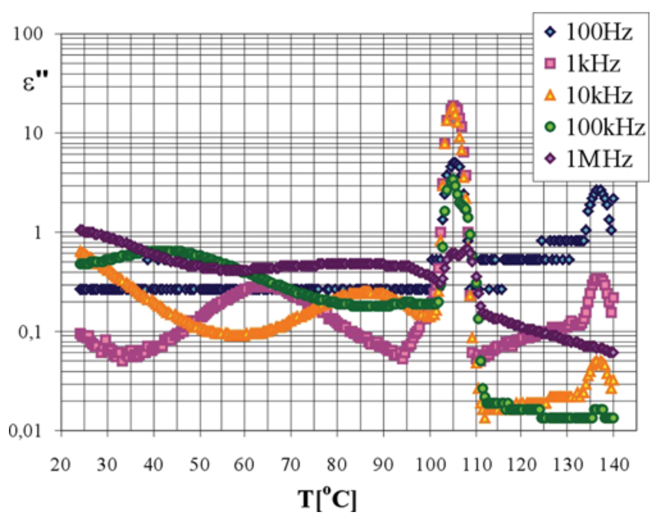

Figure 4. Imaginary part ε'' of the electric permittivity of W-1000A mixture as a function of the temperature.

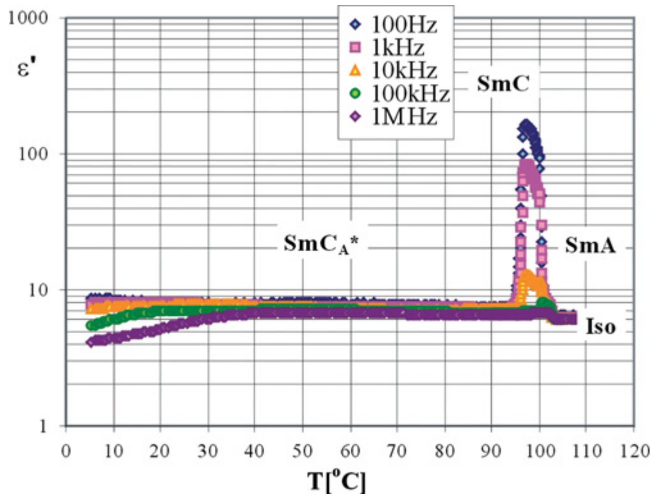

Figure 5. Real part ε' of the electric permittivity of W-1000A mixture as a function of the temperature.

imaginary part of electric permittivity ε'' for different frequencies f (Fig. 4) of the driving electric field suggest, that relaxation frequencies f_R change a lot in antiferroelectric phase and that it should be more than one mode in SmC_A^* [2].

The doping of the W-1000 mixture with homostructural, racemic compounds A-3 and B-3 caused that SmA* and SmC* phases are shifted into lower temperatures about 7–8 degrees (Figs. 5 and 7). In case of W-1000B the boardening of SmC* phase is additionally observed.

In the Figures 9, 11, 13, 15 and 16 relaxation frequencies f_R and in the Figures 10, 12 and 14 dielectric strenghts $\Delta\varepsilon$ for all modes detected in smectic phases: soft mode,

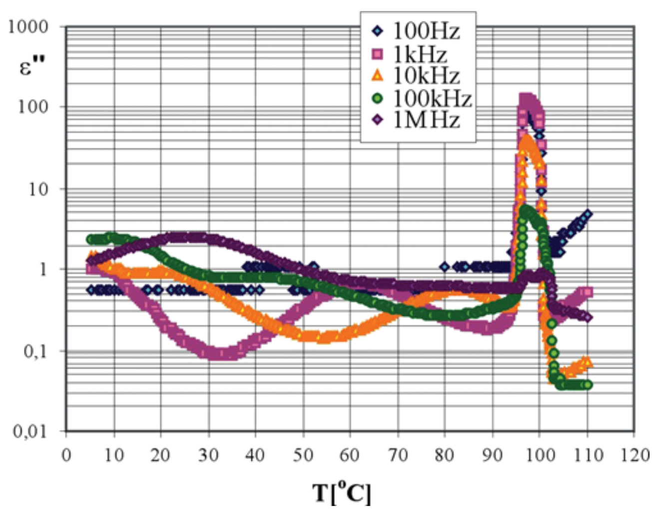

Figure 6. Imaginary part ε'' of the electric permittivity of W-1000A mixture as a function of the temperature.

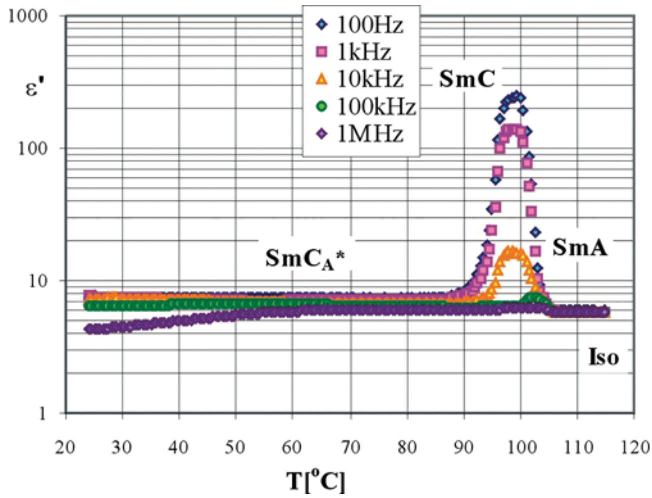

Figure 7. Real part ε' of the electric permittivity of W-1000B mixture as a function of the temperature.

Goldstone mode, P_H, P_L and X [8] modes are presented. In case of W-1000B mixture (Fig. 13) a new, never observed before mode, was detected (denoted here as Y).

To find relaxation frequencies f_R and dielectric strength $\Delta\varepsilon$ from Cole-Cole model a custom made software COLE-COLE.VEE was applied.

Several dielectric modes are detected in W-1000 mixture (Fig. 9): high frequency mode (X-mode) with relaxation frequency between 2 MHz and 10 MHz; P_H mode with relaxation frequency between 20 kHz and 1.3 MHz (slowly increasing with temperature); P_L mode with relaxation frequency between 0.2 kHz and 100 kHz; Goldstone mode with constant relaxation frequency f_R around 2-3 kHz and soft

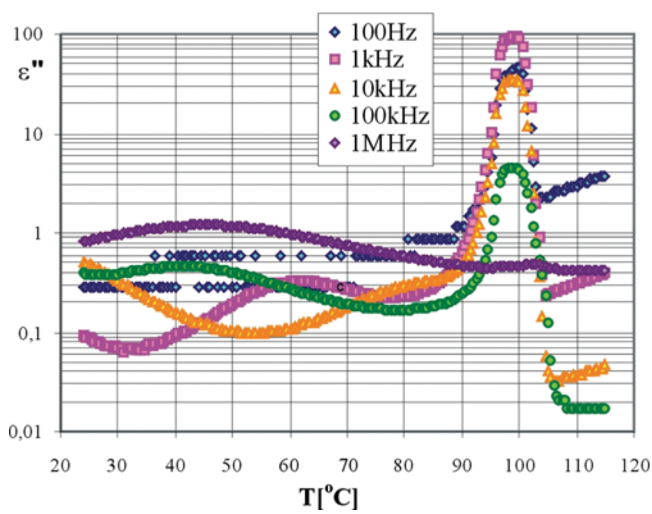

Figure 8. Imaginary part ε'' of the electric permittivity of W-1000B mixture as a function of the temperature.

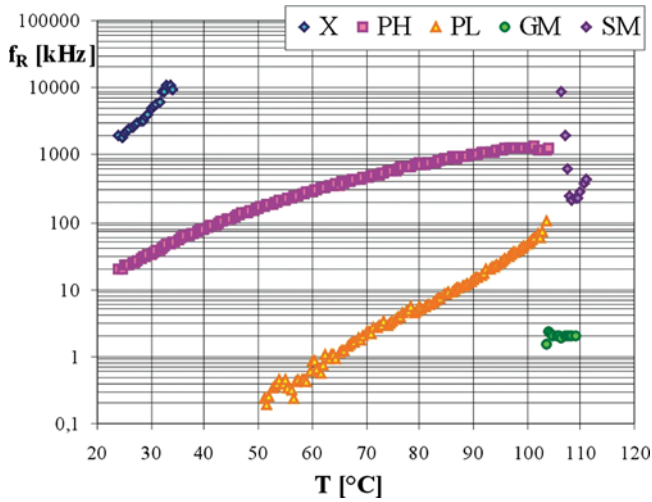

Figure 9. Relaxation frequencies f_R for W-1000 mixture for all detected modes: (X – high frequency mode in SmC_A^*, PH – P_H mode, PL – P_L mode, GM – Goldstone mode, SM – soft mode [2].

mode with frequencies decreasing from 8.5 MHz to 200 kHz in SmC* phase and increasing from 200 kHz up to 400 kHz in SmA* phase.

Relaxation frequencies of all three modes at the antiferroelectric phase (P_H, P_L and X modes) decrease when the temperature decline. All detected modes are well separated in frequency domain. Difference between relaxation frequencies of P_L and P_H modes as well as the difference between X and P_H modes are 1–2 decades. X mode does not co-exist with P_L mode however the range of the measuring frequency might be too small to register both modes simultaneously.

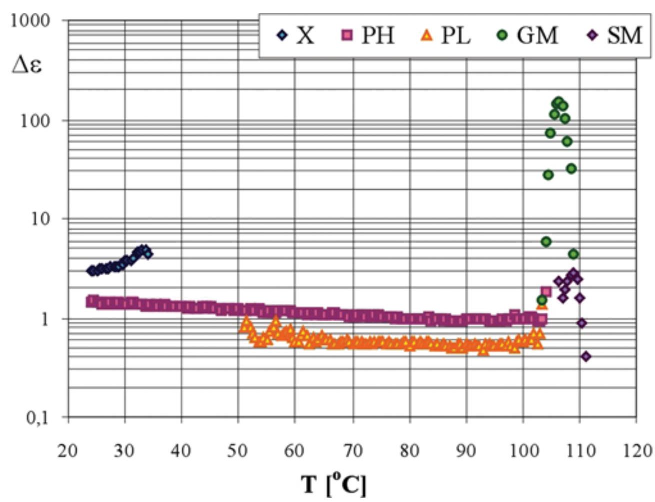

Figure 10. Dielectric strenght Δε for W-1000 mixture for all detected modes: X – high frequency mode in SmC_A^*, PH – P_H mode, PL – P_L mode, GM – Goldstone mode, SM – soft mode [2].

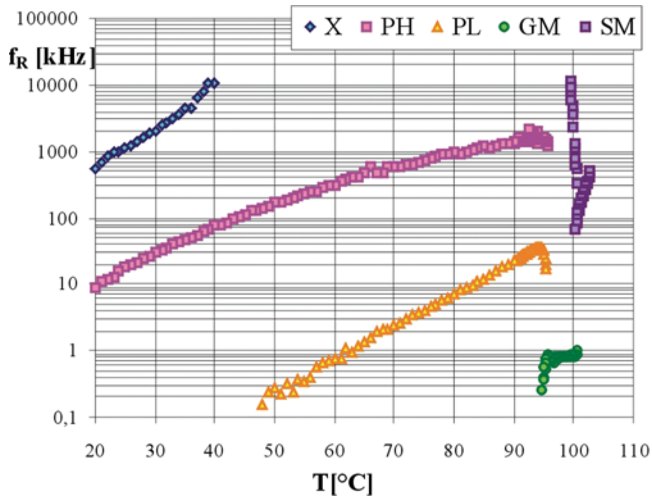

Figure 11. Relaxation frequencies f_R for W-1000A mixture for all detected modes: X – high frequency mode in SmC_A^*, PH – P_H mode, PL – P_L mode, GM – Goldstone mode, SM soft mode.

Modes detected in W-1000A (Fig. 11) and W-1000B (Fig. 13) mixtures are the same like detected in the parent mixture W-1000. X mode in the W-1000A mixture exhibits a relaxation frequency between 550 kHz and 10 MHz and in the W-1000B mixture, between 2 MHz and 50 MHz at the full temperature domain. In case of W-1000B mixture a Y mode with constant relaxation frequency f_R 8–9 MHz was observed. This mode has low dielectric strenght (Fig. 14.) so it is supposed to be a weak molecular mode in isotropic phase.

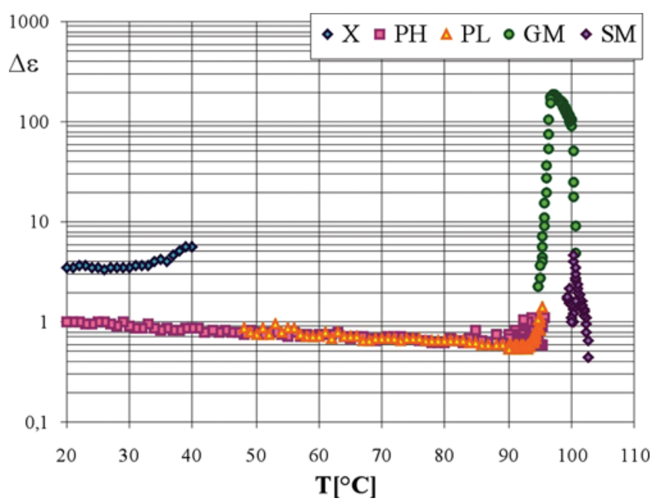

Figure 12. Dielectric strenght Δε for W-1000A mixture for all detected modes: X – high frequency mode in SmC_A^*, PH – P_H mode, PL – P_L mode, GM – Goldstone mode, SM – soft mode.

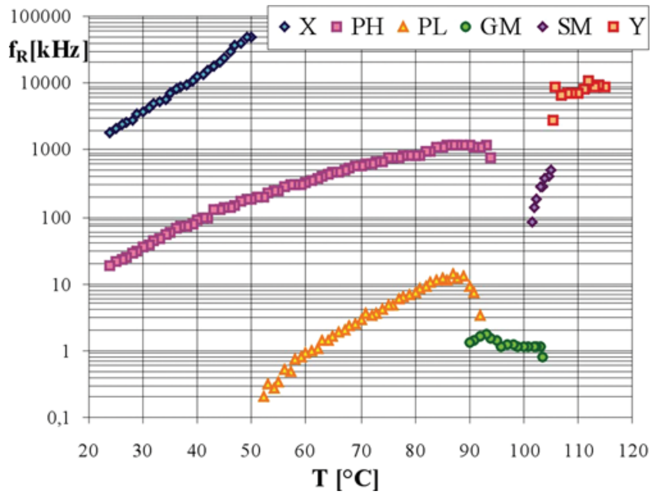

Figure 13. Relaxation frequencies f_R for W-1000B mixture for all detected modes: X – high frequency mode in SmC_A^*, PH – P_H mode, PL – P_L mode, GM – Goldstone mode, SM soft mode and Y mode.

Several dielectric modes are detected in compound W-1 (Fig. 15) and W-2 (Fig. 16): high frequency mode (X - mode), P_H mode, P_L mode, Goldstone mode and soft mode. Relaxation frequency of soft mode for W-2 component change with temperature more than relaxation frequency of soft mode for W-1 component.

The temperature dependence of the relaxation frequency of the soft mode in W-2 component is more pronounced than that in the W-1 mixture (see Figs. 15 and 16).

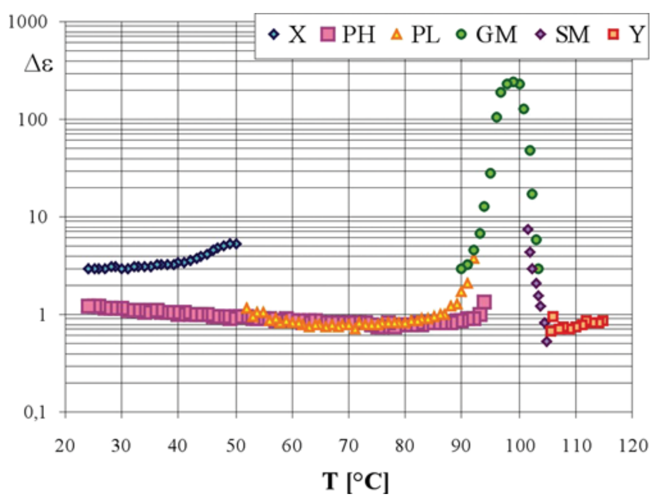

Figure 14. Dielectric strenght Δε for W-1000B mixture for all detected modes: X – high frequency mode in SmC_A^*, PH – P_H mode, PL – P_L mode, GM – Goldstone mode, SM – soft mode and Y mode.

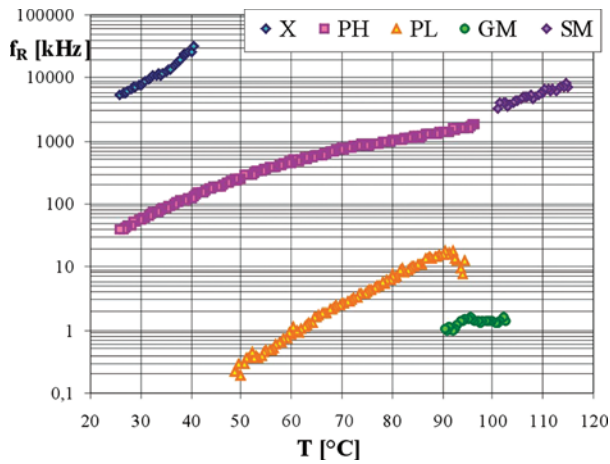

Figure 15. Relaxation frequencies f_R for W-1 compound for all detected modes: X – high frequency mode in SmC_A^*, PH – P_H mode, PL – P_L mode, GM – Goldstone mode, SM soft mode.

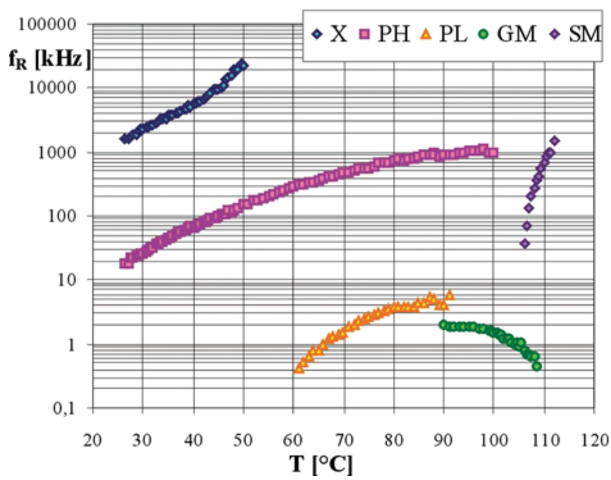

Figure 16. Relaxation frequencies f_R for W-2 compound for all detected modes: X – high frequency mode in SmC_A^*, PH – P_H mode, PL – P_L mode, GM – Goldstone mode, SM soft mode.

Nonlinear progress of the Goldstone mode in compound W-2 and its coexistence with the soft mode at the SmA^* phase is caused probably by the electroclinic effect or incidence of de Vries phase.

5. Conclusions

The doping of the parent mixture W-1000 with racemic compounds A-3 and B-3 caused a marked increase of the real part of the electric permittivity ε' at the SmC^*

phase. The another consequence of the doping with racemic compounds A-3 and B-3 is a change of temperatures of phase transition (Figs. 3, 5 and 7).

In W-1000 mixture the dielectric strenght $\Delta\varepsilon$ of P_L mode is much lower than the dielectric strenght of P_H mode. The doping caused that in W-1000A and W-1000B mixtures the dielectric strenghts $\Delta\varepsilon$ of P_L and P_H modes are similar (Figs. 12 and 14).

X mode in doped W-1000A and W-1000B mixtures exist in higher temperatures than X mode in parent W-1000 mixture.

Let us recall that the overall difference within the molecular structure of racemic dopants A-3 and B-3 is the fluorine substitution within the molecular core. This detail apparently affects the dynamics of the molecular movement within the doped mixtures.

Acknowledgment

This paper has been done in 2010 year under financial support the Polish Ministry of Sciences and Higher Education under the Key Project POIG.01.03.01-14-016/08 "New Photonic Materials and their Advanced Application."

References

[1] Piecek, W., Perkowski, P., Raszewski, Z., Morawiak, P., Żurowska, M., Dąbrowski, R., & Czupryński, K. (2010). Long pitch orthoconic antiferroelectric mixture for display applications. *Molecular Crystals & Liquid Crystals*, *525*, 160–172.

[2] Perkowski, P., Ogrodnik, K., Piecek, W., Raszewski, Z., Żurowska, M., & Dąbrowski, R. (2010). High frequency mode in a new antiferroelectric mixture. *Molecular Crystals and Liquid Crystals*, *525*, 64–70.

[3] Rudquist, P., Lagerwall, J. P. F., Meier, J. G., D'have, K., & Lagerwall, S. T. (2002). Tilt plane orientation in antiferroelectric liquid crystal cells and the origin of the pretransitional effect. *Physical Review E*, *66*, 061708.

[4] Żurowska, M., Dąbrowski, R., Dziaduszek, J., Rejmer, W., Raszewski, Z., & Piecek, W. (2010). Comparison of racemic and enantiomeric 4′-(1-methylheptyloxycarbonyl)-biphenyl 4-yl 4-[3-(2,2,3,3,4,4,4-heptafluorobutoxy) prop-1-oxy]benzoates. *Molecular Crystals Liqud Crystals*, *525*, 239–245.

[5] Żurowska, M., Dąbrowski, R., Dziaduszek, J., Czupryński, K., Skrzypek, K., & Filipowicz, M. (2008). Synthesis and mesomorphic properties of chiral esters comprising partially fluorinated alkoxyalkoxy terminal chains and a 1-methylheptyl chiral moiety. *Molecular Crystals Liquid Crystals*, *495*, 145/[497]–157/[509].

[6] Rejmer, W., Żurowska, M., Dąbrowski, R., Czupryński, K., Raszewski, Z., & Piecek, W. (2009). An influence of the fluorosubstitution and the spacer length on the phase transitions and helical pitch value in high tilted antiferroelectric esters. *Molecular Crystals Liquid Crystals*, *509*, 195/[937]–205/[947].

[7] Żurowska, M., Dąbrowski, R., Dziaduszek, J., Garbat, K., Filipowicz, M., Tykarska, M., Rejmer, W., Czupryński, K., Spadło, A., Bennis, N., & Otón, J. M. (in press). Influence of alkoxy chain length and fluorosubstitution on mesogenic and spectral properties of high tilted antiferroelectric esters. *Jurnal of Materials Chemistry*.

[8] Perkowski, P., Piecek, W., Raszewski, Z., Ogrodnik, K., Rutkowska, J., Żurowska, M. Dąbrowski, R., Kędzierski, J., & Sun, X. (2008). New high frequency dielectric mode in fluorinated antiferroelectric liquid crystals. *Ferroelectrics*, *365*, 88–94.