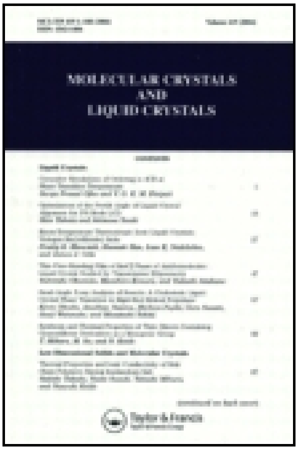

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Systems with Enhanced Antiferroelectric Phase. Phase Diagrams, Dielectric and Electro-Optic Studies

Roman Danbrowski [a], Witold Drzewiński [a], Krzysztof Czupryński [a], Sebastian Gauza [a], Krystyna Kenig [a], Wojciech Kuczyński [b] & Faustyna Goc [b]

[a] Military University of Technology, Warsaw, 00-908, Poland

[b] Institute of Molecular Physics, Polish Academy of Sciences, Poznań, 60-179, Poland

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Systems with Enhanced Antiferroelectric Phase. Phase Diagrams, Dielectric and Electro-Optic Studies

ROMAN DĄNBROWSKI[a], WITOLD DRZEWIŃSKI[a], KRZYSZTOF CZUPRYŃSKI[a], SEBASTIAN GAUZA[a], KRYSTYNA KENIG[a], WOJCIECH KUCZYŃSKI[b] and FAUSTYNA GOC[b]

[a]*Military University of Technology, Warsaw 00–908, Poland and* [b]*Institute of Molecular Physics, Polish Academy of Sciences, Poznań 60–179, Poland*

The phase diagrams, dielectric permittivity, electro-optic response for field induced antiferroelectric-ferroelectric transition of mixtures containing compounds with a partially fluorinated terminal chain are shown. V-shaped switching is observed in such mixtures.

Keywords: antiferroelectric liquid crystals; bi- and multicomponent mixtures; phase diagrams; dielectric permittivity; V-shaped switching

INTRODUCTION

The discovery of thresholdless antiferroelectric LC by Fukuda's team giving V-shaped switching[1,2] involves a great interest for further searching for such materials because of their great usefulness for active matrix displays[3]. These materials having reduced interlayer correlations were recently called as disordered (random) or frustrated antiferroelectrics (SmC_R^* or FR)[4]. V-shaped switching is considered to be caused by thermally fluctuated barrier between the antiferroelectric and ferroelectric transition[4], although Rudquist et al. proposed other explanation of this feature[5].

A limited number of LC materials showing V-shaped switching have been disclosed up to now. They belong mainly to two types of the mixture materials. The first one (developed by Mitsubishi) consists of the compounds showing SmC_γ^* (ferri- phase) in a broad temperature range as the main phase. The second one (developed by Mitsui) contains two types of components: the first one is a compound having SmC_A^* phase in a broad temperature range and the other one is a compound having SmC_γ^* phase. In these mixtures the phase situation is very labile and the temperature transition and phase sequence can be easily changed upon experimental conditions[6]. It is interesting to know whether only such labile systems exhibit V-shaped switching or also other systems are possible to find. Recently we have synthesized chiral esters with partially fluorinated chain[7]. Their unusual optic properties were found[8] and their ability to induce SmC_A^* was observed[9]. For these reason we have been started systematic studies of different bicomponent systems containing the fluorinated compounds.

In this work we present the phase diagram, dielectric and electro-optic studies of the bicomponent system which consists of the compounds 1-4 as well as multicomponent system A-B.

(S) $\mathrm{F_{13}C_6CH_2CH_2O\text{-}Ph\text{-}Ph\text{-}COO\text{-}Ph\text{-}COOC^*H(CH_3)C_6H_{13}}$ 1

$\mathrm{Cr_1} \xrightarrow[3.02]{80.7} \mathrm{Cr} \xrightarrow[4.60]{98.1} \mathrm{SmC_\beta^*} \xrightarrow[0.20]{148.1} \mathrm{SmA} \xrightarrow[1.13]{183.6} \mathrm{Iso}$

(S) $\mathrm{F_3CCH_2OC_3H_6O\text{-}Ph\text{-}Ph\text{-}COO\text{-}Ph\text{-}COOC^*H(CH_3)C_6H_{13}}$ 2

$\mathrm{Cr} \xrightarrow[8.63]{106.9} \mathrm{SmC_A^*} \xrightarrow[0.10]{124.5} \mathrm{SmA} \xrightarrow[1.29]{134.0} \mathrm{Iso}$

(S) $\mathrm{H_{17}C_8O\text{-}Ph\text{-}Ph\text{-}COO\text{-}Ph\text{-}COOC^*H(CH_3)C_7H_{15}}$ 3

$\mathrm{Cr_1} \xrightarrow[2.03]{60.8} \mathrm{Cr} \xrightarrow[5.63]{79.7} (\mathrm{SmI_A^*} \xrightarrow[0.31]{65.8)} \mathrm{SmC_\beta^*} \xrightarrow[0.007]{118.4} \mathrm{SmC_\alpha^*} \xrightarrow[0.012]{118.7} \mathrm{SmA} \xrightarrow[1.45]{144.1} \mathrm{Iso}$

(S) $H_{17}C_8O\text{-}Ph\text{-}COO\text{-}Ph\text{-}COO\text{-}Ph\text{-}COOC^*H(CH_3)C_6H_{13}$ **4**

$$\mathrm{Cr}\ \frac{87.4}{9.53}\ (\mathrm{SmC_A}^*\ \underline{60.5)}\ \mathrm{SmC_\gamma}^*\ \frac{89.7}{0.001}\ \mathrm{SmC_\beta}^*\ \frac{94.5}{0.008}\ \mathrm{SmC_\alpha}^*\ \frac{96.2}{0.007}\ \mathrm{SmA}\ \frac{140.9}{1.46}\ \mathrm{Iso}$$

mixture A	wt. %
$F_7C_3COOC_3H_6OPhPhCOOPhCOOC^*H(CH_3)C_6H_{13}$	16,12
$F_7C_3COOC_4H_8OPhPhCOOPhCOOC^*H(CH_3)C_6H_{13}$	31,61
$F_{15}C_7COOC_3H_6OPhPhCOOPhCOOC^*H(CH_3)C_6H_{13}$	28,58
$F_3CCH_2CH_2OC_3H_6OPhPhCOOPhCOOC^*H(CH_3)C_6H_{13}$	4,27
$F_9C_4COOC_3H_6OPhPhCOOPhCOOC^*H(CH_3)C_6H_{13}$	19,42

Cr 44 SmC_A^* 120.5 SmC^* 124 SmA 135 Iso

mixture B	wt. %
$F_{13}C_6CH_2CH_2OPhPhCOOPhCOOC^*H(CH_3)C_6H_{13}$	16,53
$F_{13}C_6CH_2CH_2OPhCOOPhPhCOOC^*H(CH_3)C_6H_{13}$	16,02
$F_{13}C_6CH_2CH_2OPhCOOPhCOOC^*H(CH_3)C_6H_{13}$	49,20
$F_{17}C_8CH_2CH_2OPhCOOPhCOOC^*H(CH_3)C_6H_{13}$	18,25

Cr 40 SmC^* 63 SmA 95-109 Iso

The experimental procedure is the same as it was described in the parallel work[10].

RESULTS

Phase diagram studies

Phase diagrams of the studied bicomponent and multicomponent systems are listed in Figures 1 and 2a. Each mixture contains the component with the SmC_A^* phase and the component with the SmC_β^* phase.

Mixtures A-B exhibit smectic layers tilted higher than 42° at 50°C below the SmC_β^*-SmA transition, an example is presented in Figure 2b.

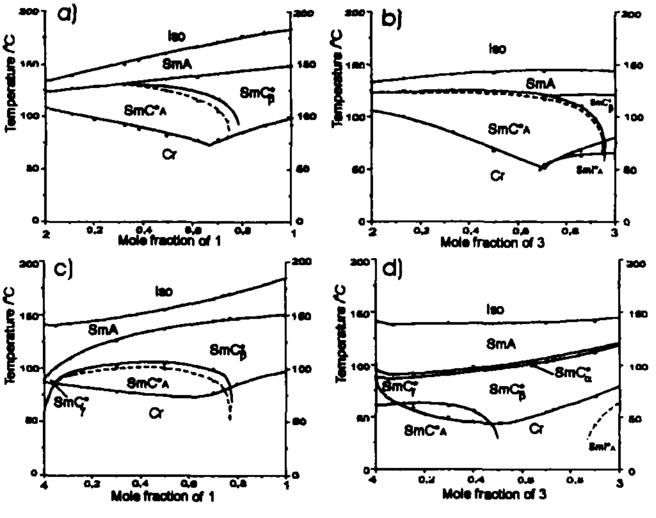

FIGURE 1 Comparison of the phase diagrams of bicomponent mixtures (from microscopic observation in thin layer): a - when both components are fluorinated compounds, b and c - one component is fluorinated compound and another one is hydrogenated and d - when both components are hydrogenous compounds
— heating, - - -cooling.

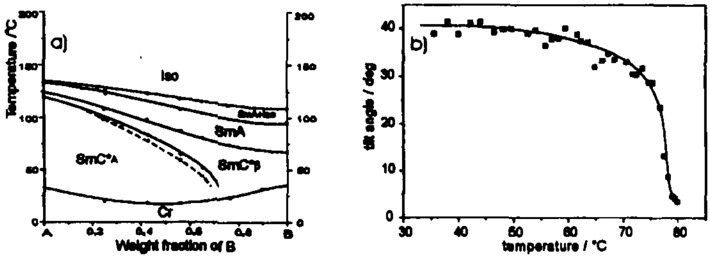

FIGURE 2 a - The phase diagram of the system A-B; b - dependence of apparent tilt angle upon temperature from optical measurement for mixture A-B with 0.65 weight fraction of B.

Dielectric studies

Figures 3 and 4 show the temperature dependence of the dielectric permittivity of 1-4 and A-B mixtures respectively as the typical examples of observed behavior.

A broad temperature hysteresis for the transition SmC$_\beta$*-SmC$_A$* is observed in the dielectric permittivity measurements during heating and cooling cycles for these concentrations of bicomponent and multicomponent mixtures where a rapid increase or decrease of the SmC$_A$* stability phase occurs, see Figures 3a, 3c and 4b. The SmC$_\beta$* phase exists in much lower temperatures during cooling than heating.

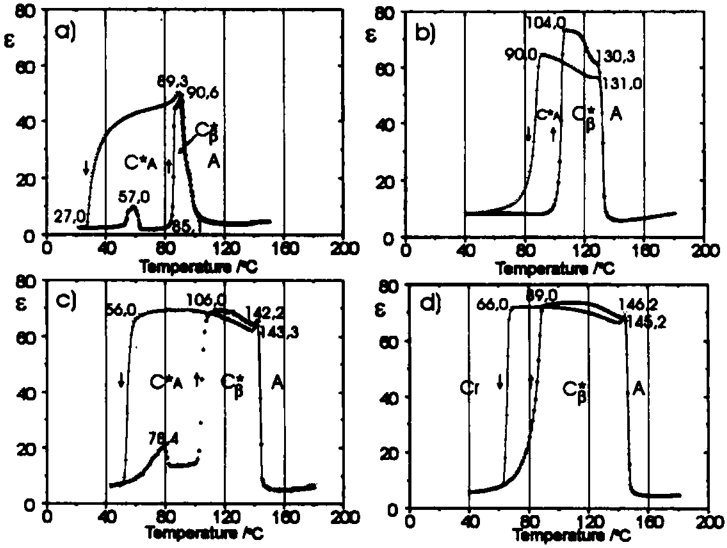

FIGURE 3 Temperature dependence of the dielectric permittivity measured at frequency 440 Hz in mixture 1-4 for the mole fractions of 1 respectively a - 0.05, b - 0.4, c - 0.68 and d - 0.80 during heating and cooling cycles.

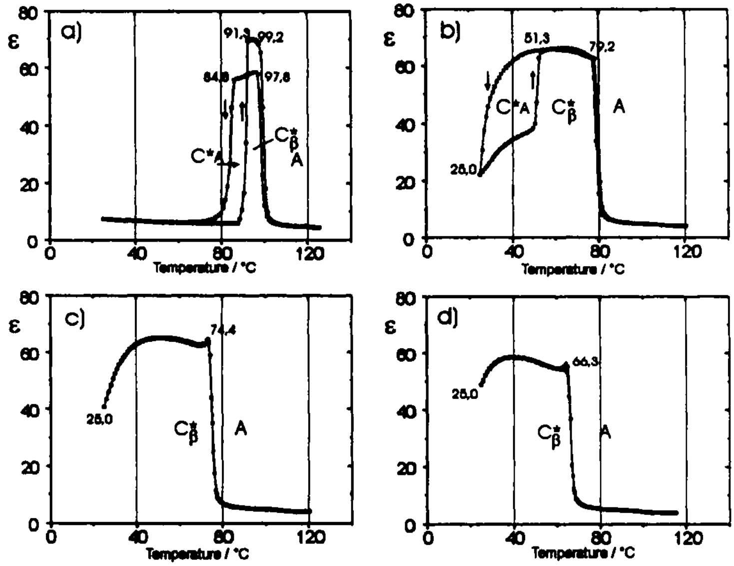

FIGURE 4 Temperature dependence of the dielectric permittivity measured at frequency 440 Hz in mixture A-B for the concentrations of B in weight fraction a – 0.05, b – 0.65, c – 0.75 and d – 1.0.

Switching properties

In the mixture 2-3 with mole fraction 0.95 of 3 a typical tristable switching due to the field induced antiferroelectric-ferroelectric transition is observed at the low temperature (50°C and below) and at low frequency - 0.03 Hz, see Figure 5. At the temperature region, for higher frequencies the reverse transition from ferroelectric state to the antiferroelectric one has no time to occur during field pulse and only direct transition from ferroelectric (+) state to the ferroelectric (-) state happens with normal W-shaped EO response. The threshold voltage of the AF-F transition measured at low frequency 0.03 Hz decreases, when the temperature increases and the observed hysteresis is getting smaller

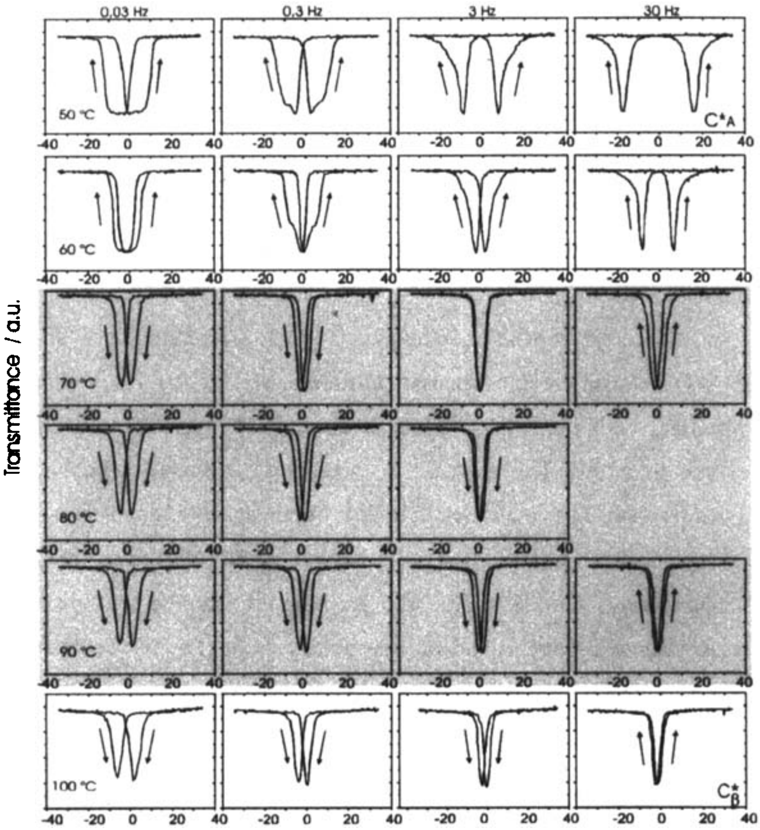

FIGURE 5 Electro-optic switching at various temperatures and various frequencies in mixture 2-3 with mole fraction 0.95 of 3; $\mathrm{SmC}_A^* \rightleftarrows \mathrm{SmC}_\beta^*$ equilibrium region from the dielectric observations is marked by gray color.

and the EO takes a W-shaped form with the opposite hysteresis. Typical no hysteresis V-shaped switching appears only above 60°C at the frequency 3 Hz.

The bicomponent system 1-4 for the mole fraction 0.05 of 1 shows at temperature 50°C and at the low frequency a nearly ideal V-shaped switching, Figure 6 – Ia, and for higher frequency (30 Hz) W-shaped switching with normal hysteresis. For small frequency 0.3 Hz W-shaped switching with opposite hysteresis appears above temperature 60°C, that is still in the temperature range of SmC_{β}^{*}-SmC_{A}^{*} equilibrium, Figure 6 – IIa.

The mixture with mole fraction 0.4 of 1 at the frequency 0.03 Hz shows irregular crossed opposite hysteresis and at 0.3 Hz V-shaped switching with normal hysteresis is developed, Figure 6 – Ib up to temperature 70°C. The mixture 1-4 containing fluorinated compound in mole fraction 0.68 shows the tristable switching with small threshold voltage and high saturation voltage but small hysteresis, at low temperature, Figure 6 – IIc. The increase of temperature, involves narrowing of hysteresis and only switching from (F+) to (F-) state is observed above 70°C with opposite W-shaped hysteresis for both, low and high, frequencies.

The pure component B and the mixture A-B with the 0.75 and 0.70 weight fraction of B having only SmC_{β}^{*} phase in all studied temperature ranges as well as that with 0.65 weight fraction of B having SmC_{A}^{*}-SmC_{β}^{*} phases in equilibrium between 25 and 51°C show at the temperature 30°C and at different frequencies the same electro-optical responses. At low frequency the V-shaped switching is almost ideal or only a small opposite hysteresis is observed. At higher frequencies W-shaped switching with normal hysteresis is observed, Figure 7 – Ia, b, c and d.

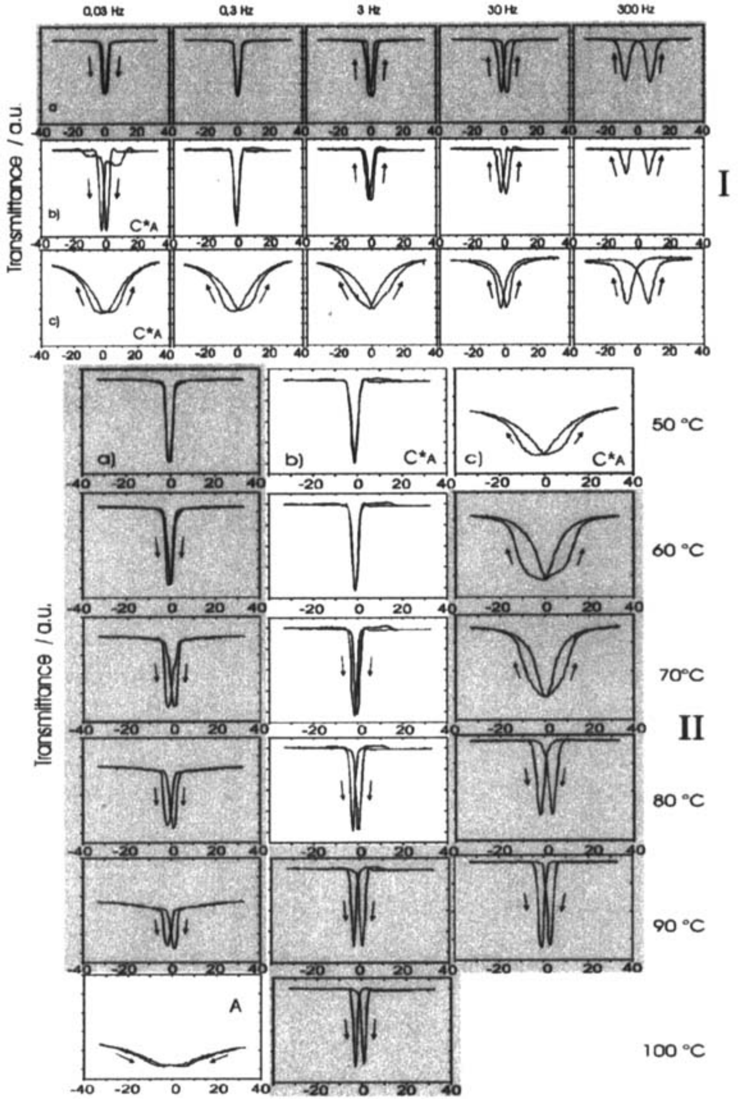

FIGURE 6 Electro-optic switching at the temperature 50 °C and various frequencies – I; and at various temperatures and frequency 0.3 Hz – II in mixture 1-4 with mole fraction of 1 a - 0.05, b - 0.4 and c - 0.68; gray color - $SmC_A^* \rightleftarrows SmC_\beta^*$ region.

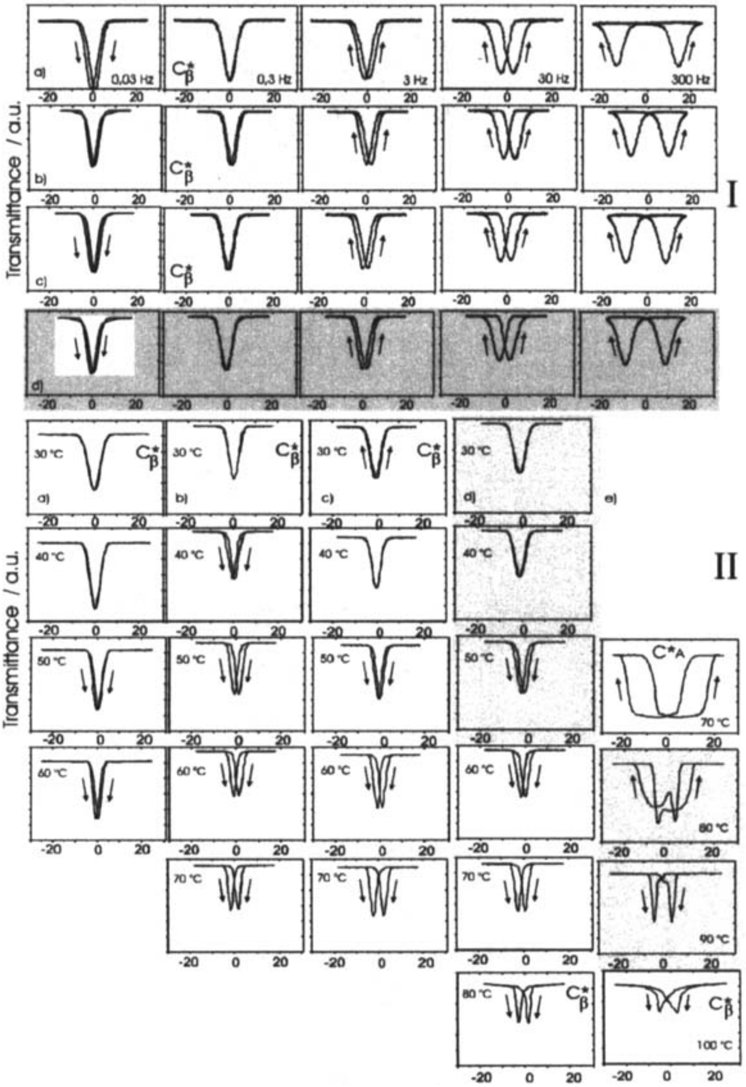

FIGURE 7 Electro-optic switching at the temperature 30°C and various frequencies – I and at frequency 0.3 Hz and different temperatures – II in mixture A-B a – *1.0*, b – *0.75*, c – *0.70*, d – *0.65* and e – *0.50* weight fraction of B; gray color - $SmC_A^* \rightleftarrows SmC_\beta^*$ region

The same switching character is observed for these mixtures up to temperature 50°C and above this temperature switching starts to take W-shape switching with the increasing opposite hysteresis.

The mixture A-B with 50 wt. fraction of B has the large threshold voltage for the AF-F transition at the temperature 30° and for the used experimental condition it can be measured below 60°C. At this temperature the mixture shows normal triple switching which transforms to double switching F(+) to F(-) states above 85°C.

DISCUSSION AND CONCLUSIONS

Five different chiral tilted smectic systems were investigated. The strongest ability to the enhancement of the SmC_A^* phase was observed in the systems wherein the compound with partially fluorinated terminal chain situated in the position opposite to the chiral center was mixed with the compound having hydrogenous terminal chain.

In such systems a concentration range, where the SmC_β^* and SmC_A^* phases may coexist in a large temperature range during cooling and heating cycles was found. This is perfectly seen in dielectric permittivity measurements. Therefore such mixtures can be termed as a frustrated SmC_A^* material. The frustration is especially well seen in the mixtures consisted of a component having the SmC_γ^* phase above the SmC_A^* phase (see the system 1-4) but it is not necessary for exhibition of that property. All systems investigated here with the SmC_A^* and SmC_β^* phases in equilibrium, showed the V-shaped switching but the same switching was also observed in mixtures having only the SmC^*

phase (see for example mixture B and part of mixtures A-B) as well as in the mixtures with the stable SmC_A^* phase (see system 1-4 with mole fraction 0.4 of 1 at the low temperature). Similar cases were also observed by the others[5].

For these reasons the frustrated state of SmC_A^* phase is rather not responsible for V-shaped EO response but such behavior results rather in space charge effects in the twisted strong polar SmC^* structure, what was recently postulated by Rudquist et al.[5]. All the investigated here V-switching LC materials in the electric filed dynamic conditions exist rather in the SmC_β^* phase (ferroelectric). This phase does not have possibility to change into the SmC_A^* phase during the field cycle because that needs longer time than the pulse time used.

From this point of view the material having SmC_A^* phase and simultaneously able to show V-shaped switching should possess such SmC_A^* phase in which the antiferroelectric order is not strong and can be easily destroyed by small electric field. In the investigated systems the V-shaped switching was observed in the temperature range and under such frequency condition wherein V-shaped opposite hysteresis was transformed via V-shaped no hysteresis to V-shaped normal hysteresis. Recently Chandani et al. showed[11] that it results from the ionic processes which occur during switching (the charge accumulation and associated reverse field).

We showed here that V-switching materials are not exotic ones and may be easy found in many bi- and multicomponent systems composed also of the compounds not having SmC_γ^* phase. The materials described by us show the frequency and temperature dependence very similar to the Inui or Mitsui type of V-shaped switching materials. The switching properties of our mixtures may be easily adjusted by the change of components properties. Also LC material with tilt angle 45° can be prepared.

Acknowledgments

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