

# ON THE COEXISTENCE OF $\text{SmC}^*$ AND $\text{SmC}_A^*$ PHASES IN BINARY CHIRAL-DOPANT ANTIFERROELECTRIC MIXTURES

J. P. F. LAGERWALL, D. D. PARGHI<sup>†</sup>, G. HEPPKE<sup>†</sup>

Chalmers University of Technology, 412 96 Göteborg, Sweden.

<sup>†</sup>INSI, TU Berlin, Str. des 17 Juni 135, D-10623 Berlin, Germany.

## ABSTRACT

We present the results from investigations on a series of binary chiral-dopant liquid-crystalline mixtures. The racemic host materials possess tilted smectic phases with varying strengths of synclinc and anticlinc ordering ( $\text{SmC}$  and  $\text{SmC}_{\text{alt}}$  phases respectively). The dopants used were either a strongly synclinc-favouring non liquid-crystalline chiral material (commonly used in FLC chiral-dopant mixtures) or a strongly anticlinc (antiferroelectric) material ((*S*)-MHPOBC). The electrooptic and dielectric properties of the mixtures were investigated in test cells of different thickness and the influence of each mixture component on the observed physical properties is discussed.

Keywords      Ferroelectric, antiferroelectric, phase coexistence,  
cell thickness, electrooptics, dielectric spectroscopy.

## INTRODUCTION

Surface stabilised ferroelectric [1] and antiferroelectric [2] liquid crystals, and the observed delicate balance between ferroelectric and antiferroelectric order, have recently stimulated studies in very thin cells and the effect of surface actions on the various kinds of order. These studies are equally relevant for display modes using the Deformed Helix [3], Twisted Smectic  $C^*$  [4] and V-Shaped Switching [5] effects.

A feature common to all these concepts is the presence of

alignment layers in the cells necessary to stabilise the desired geometry of the chiral smectic phase.

For use in any of the above devices mixtures of different materials are required in order to fully exploit the potential offered by liquid crystals exhibiting the  $\text{SmC}^*$  or  $\text{SmC}_A^*$  phase. The usual technique for preparing a mixture for use in an SS-FLCD involves the doping of a pre-selected achiral  $\text{SmC}$ -forming host mixture with a chiral material. This induces a spontaneous polarisation and consequently ferroelectricity (if the mixture is placed in a sufficiently thin cell) into the mixture and makes it “switchable” [6]. In a similar manner, by doping a racemic or achiral host possessing a  $\text{SmC}_{\text{alt}}$  phase with a suitable chiral material, antiferroelectricity can be induced in the material [7]. Recently, two such model binary mixtures were prepared and their electrooptic and dielectric behaviour was studied [8]. Certain samples showed behaviour in the  $\text{SmC}_A^*$  phase that was not typical for an antiferroelectric liquid crystal. In fact by comparing textures, electrooptic switching behaviour and dielectric spectra, it was clear that a strong coexistence of  $\text{SmC}_A^*$  and  $\text{SmC}^*$  phases was present. Similar behaviour has been reported earlier in pure substances by Moritake *et al.* and Hatano *et al.* [9].

In this paper we have made a thorough study of several binary chiral-dopant antiferroelectric systems in order to map the influence of dopant, host material, and cell thickness on the behaviour of the induced  $\text{SmC}^*$  and  $\text{SmC}_A^*$  phases. The samples were investigated using optical microscopy, electrooptic switching studies, and dielectric spectroscopy.

## RESULTS AND DISCUSSION

### 1. Mesomorphic properties

The materials chosen as hosts were (*R/S*)-8F1M6, (*R/S*)-10F1M7, and (*R/S*)-10F2E7 (FIGURE 1), which range from strongly synclitic to strongly anticlitic. The dopants used were 10% (*S*)-IGS97 [10] and 15% (*S*)-MHPOBC [11] (by weight). The first is a standard non liquid-crystalline (“ferroelectric-like”) dopant used in chiral-dopant FLC mixtures and strongly promotes the  $\text{SmC}^*$  phase, and the latter strongly promotes the  $\text{SmC}_A^*$  phase. The combinations of dopant and host types in the mixtures are summarised in TABLE 1. TABLE 2 shows the transition temperatures of the mixtures.

The (*R/S*)-10F1M7 and (*R/S*)-10F2E7 hosts possess room temperature  $\text{SmC}_A$  phases and (*R/S*)-8F1M6 possesses a  $\text{SmC}$  phase and an as-yet unclassified hexatic phase (“SmX”, most likely  $\text{SmI}$  or  $\text{SmF}$ ).

## CHIRAL-DOPANT AFLC MIXTURES

FIGURE 1 Structures and phase sequences (determined by optical microscopy and DSC) of the racemic host materials.

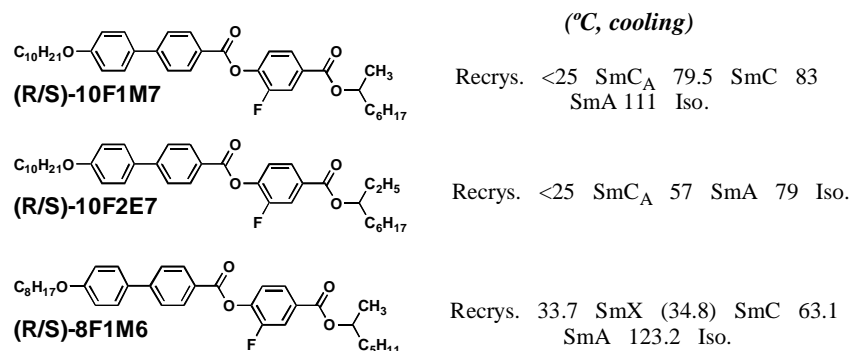


TABLE 1 Summary of the types of components present in the binary chiral-dopant mixtures.

Mixture	<i>d o p a n t</i>		<i>h o s t</i>	
	AFO ( <i>(S)</i> -MHPOBC)	“FO” ( <i>(S)</i> -IGS97)	Synclinic (SmC)	Anticlinic (SmC <sub>A</sub> )
CDMix1	•	-	•	•
CDMix2	-	•	•	•
CDMix3	•	-	-	•
CDMix4	-	•	-	•
CDMix5	•	-	•	-
CDMix6	-	•	•	-

TABLE 2 Transition temperatures and phase sequence of the binary chiral-dopant mixtures.

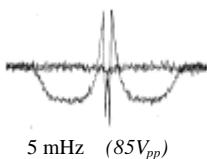
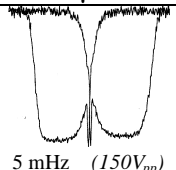
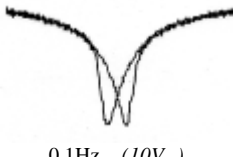
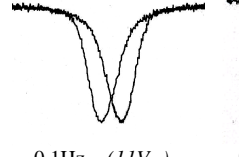
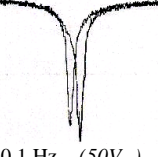
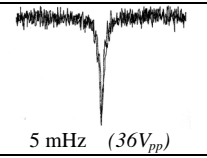
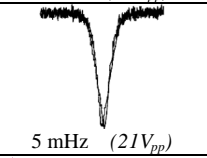
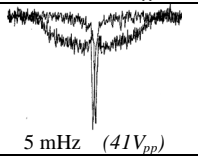
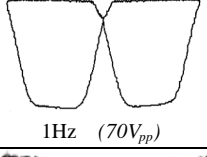
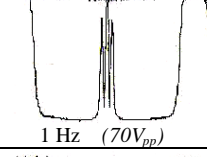
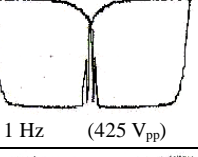
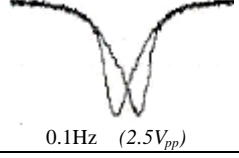
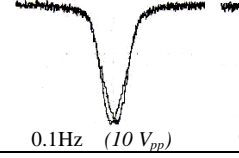
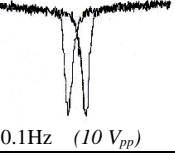
Mixture	Rec	SmX*	SmC <sub>A</sub> *	SmC*	SmA*	I
CDMix1	• < 25	-	• 82.6	• 87.1	• 116.1	•
CDMix2	• < 25	-	• 48.4	- 59.0	• 101.5	•
CDMix3	• < 25	-	• 67.5	-	- 91.8	•
CDMix4	• < 25	-	• 46.9	-	- 60.3	•
CDMix5	• 28	• (34)	-	• 70	• 124.4	•
CDMix6	• < 25	• < 25	-	• 41.3	• 110	•

The mixtures doped with the “ferroelectric-like” material, (*S*)-IGS97, exhibit a greater decrease in transition temperatures for all the observed phases in comparison to the undoped hosts. This is no doubt a consequence of the non liquid-crystalline nature of the dopant material.

2. Electrooptic Measurements

The electrooptic behaviour of the mixtures were investigated in “10 $\mu\text{m}$ ” EHC parallel-aligned cells, and 2 $\mu\text{m}$  self-made and 5 $\mu\text{m}$  Linkam antiparallel-aligned cells. TABLE 3 shows examples of the transmission vs. applied field curves for the antiferroelectric-dopant and “ferroelectric”-dopant mixtures obtained at different frequencies. The mixtures were studied at room temperature, thus nominally in the SmC<sub>A</sub>\* phase, except for **CDMix5** and **CDMix6**, which were studied at 40 °C (in the SmC\* phase, above the transition to the SmX\* phase).

TABLE 3 Transmission vs. applied field curves obtained for the antiferroelectric-dopant and “ferroelectric”-dopant binary mixtures.

	Mixture	2 $\mu\text{m}$	5 $\mu\text{m}$	“10 $\mu\text{m}$ ”
Antiferroelectric - dopant mixtures	<b>CDMix1</b> (28 °C)	 5 mHz (85V <sub>pp</sub> )	 5 mHz (150V <sub>pp</sub> )	<i>Threshold too high for switching</i>
	<b>CDMix3</b> (30 °C)	<i>Threshold too high for switching</i>		
	<b>CDMix5</b> (40 °C)	 0.1Hz (10V <sub>pp</sub> )	 0.1Hz (11V <sub>pp</sub> )	 0.1 Hz (50V <sub>pp</sub> )
“Ferroelectric” - dopant mixtures	<b>CDMix2</b> (29 °C)	 5 mHz (36V <sub>pp</sub> )	 5 mHz (21V <sub>pp</sub> )	 5 mHz (41V <sub>pp</sub> )
	<b>CDMix4</b> (28 °C)	 1Hz (70V <sub>pp</sub> )	 1 Hz (70V <sub>pp</sub> )	 1 Hz (425 V <sub>pp</sub> )
	<b>CDMix6</b> (40 °C)	 0.1Hz (2.5V <sub>pp</sub> )	 0.1Hz (10 V <sub>pp</sub> )	 0.1Hz (10 V <sub>pp</sub> )

## CHIRAL-DOPANT AFLC MIXTURES

Most of the mixtures showed electrooptic switching under applied fields of suitable magnitude. The threshold for switching to the ferroelectric state from the antiferroelectric state of **CDMix1** was found to be too high to be safely reached in the “10 $\mu\text{m}$ ” cell. This was in contrast to the low threshold for switching observed in **CDMix2**, which was doped with a non liquid-crystalline “ferroelectric-like” dopant. The reason for this difference is no doubt due to the high stability conferred into the mixture by the antiferroelectric dopant ((*S*)-MHPOBC) in **CDMix1**. The unusual appearance of the curve for this mixture in the 2  $\mu\text{m}$ -thick cell is most likely due to a birefringence effect. The threshold for **CDMix3** was found to be too high to permit any clear electrooptic switching to take place in any thickness of cells studied. This is more-than-likely due to a combination of the high stability of the ethylheptyl-substituted host material in comparison to the methylheptyl-substituted material [12]. Clear tristate switching was, however, observed in all cells of **CDMix4** which contained the “ferroelectric-like” dopant.

The curves obtained for the mixtures containing the SmC host material (**CDMix5** and **CDMix6**) are similar to each other. The type of dopant in this case appears to have little effect on the resultant mixture.

Out of all of the mixtures **CDMix2** displayed the most unusual switching behaviour. Although the mixture was found to possess both a SmC\* and a SmC<sub>A</sub>\* phase in the bulk (*ie.* on a glass microscope slide) no contribution from antiferroelectric switching is observed in either the 2 $\mu\text{m}$  or 5 $\mu\text{m}$ -thick cells. At very low frequencies (5mHz) in these cells the switching resembles hysteresis-free switching of a SmC\* phase. Only in the thick cell (“10 $\mu\text{m}$ ”) can a small contribution from antiferroelectric (tristate) switching be observed, at a very low frequency. This behaviour was recently found to be due to a form of coexistence between the SmC\* and SmC<sub>A</sub>\* phases [8]. The optical texture of a 4  $\mu\text{m}$  cell containing CDMix2, in which the coexistence is observed as ferroelectric and antiferroelectric regions, is shown in FIGURE 2. This texture was found to remain unchanged after storing the cell at room temperature for several weeks (without an applied field), confirming that the coexistence is indeed thermodynamically stable in this thin cell and not a supercooling effect.

### *Summary of Electrooptic Measurements*

Mixtures containing the “ferroelectric-like” dopant generally possess lower thresholds for switching than the equivalent mixtures containing the antiferroelectric dopant, regardless of the type of host. The cell thickness appears to play a key role in governing the nature of the switching in mixtures possessing both SmC\* and SmC<sub>A</sub>\* phases.

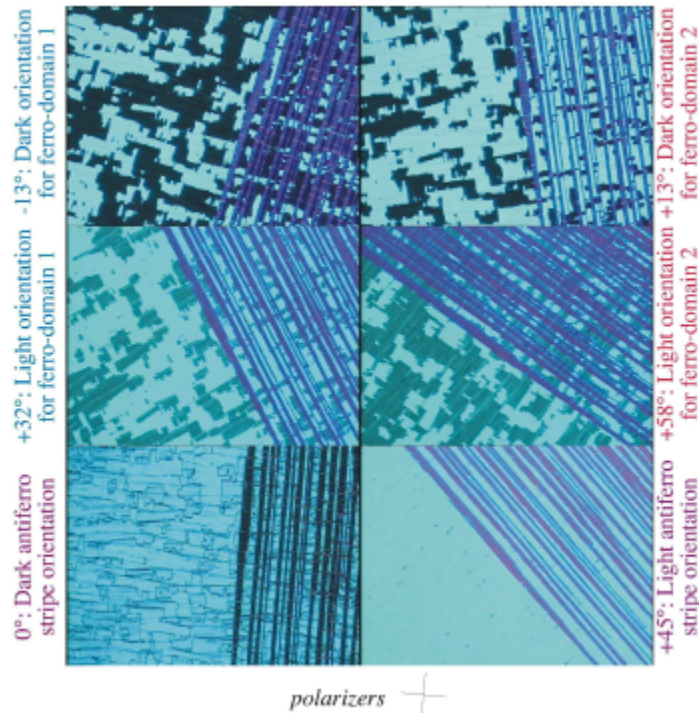


FIGURE 2 Optical texture of **CDMix2** in a 4  $\mu\text{m}$ -thick planar cell at room temperature (through crossed polarisers). The coexistent ferroelectric and antiferroelectric regions are clearly distinguishable (the tilt angle is  $13^\circ$ ).

### 3. Dielectric Spectroscopy Studies

All measurements were carried out in planar orientation with a measuring amplitude of 0.1-0.4V (HP4192A bridge). The cells used were 25  $\mu\text{m}$  EHC cells, with parallel rubbed polyimide, and self-made 2  $\mu\text{m}$ , 4  $\mu\text{m}$  and 23  $\mu\text{m}$ -thick cells, with anti-parallel rubbed polyimide.

#### *Antiferroelectric-Dopant Mixtures*

In **CDMix1**, *i.e.* the combination of a host with both anti- and synclinic phases with an antiferroelectric dopant, we measured a normal response in all phases ( $\text{SmA}^*$ ,  $\text{SmC}^*$  and  $\text{SmC}_A^*$ ). In the thick (25  $\mu\text{m}$ ) cell the transitions between the phases were very sharp, while in the 4  $\mu\text{m}$  cell we detected a very slight coexistence of the  $\text{SmC}^*$  phase into the  $\text{SmC}_A^*$  temperature region on cooling.

On changing to a strongly anticlinic host (**CDMix3**) the chiral mixture featured no  $\text{SmC}^*$  phase as expected. The transition  $\text{SmA}^*$ - $\text{SmC}_A^*$  was detected by a very weak soft mode. At lower temperatures

## CHIRAL-DOPANT AFLC MIXTURES

the lower frequency antiferroelectric mode (normally attributed to the molecular reorientation around the short axis) clearly distinguished the  $\text{SmC}_A^*$  phase in the thick ( $23\ \mu\text{m}$ ) cell. The spectrum for the  $2\ \mu\text{m}$  cell was virtually featureless and only a very weak soft mode could be detected at the  $\text{SmA}^*$ - $\text{SmC}_A^*$  transition. No indication of phase coexistence was observed in either cell.

The combination of strictly synclitic host and antiferroelectric dopant in **CDMix5** produced a chiral mixture which featured three different phases above room temperature:  $\text{SmA}^*$ ,  $\text{SmC}^*$  and  $\text{SmX}^*$ . The latter phase is a higher order smectic phase, the identity of which is not as yet clarified, but it is probably  $\text{SmI}^*$  or  $\text{SmF}^*$ . In the dielectric spectrum of this mixture (FIGURE 3) the broad  $\text{SmC}^*$  phase was distinguished by the azimuthal mode (often referred to as Goldstone mode) which was apparent in both cells. However, while this mode was strong and of low frequency in the  $23\ \mu\text{m}$  cell, it was markedly weaker, and about one order of magnitude higher in frequency, for the same mixture in the  $2\ \mu\text{m}$  cell.

Below the  $\text{SmC}^*$  phase the  $\text{SmX}^*$  phase was distinguished by a weak absorption in the kHz region. Approximately  $5\ ^\circ\text{C}$  above the  $\text{SmC}^*$ - $\text{SmX}^*$  transition, the azimuthal mode featured a sudden drop in intensity in both cells on cooling. This was probably an effect of the supercooling of the  $\text{SmC}^*$  phase; on heating, the  $\text{SmX}^*$ - $\text{SmC}^*$  transition was observed approximately  $10\ ^\circ\text{C}$  above the  $T_{\text{SmC}^*-\text{SmX}^*}$  value obtained on cooling.

By applying a DC-bias all absorptions were easily quenched. At a bias field of  $7.5\text{V}/\mu\text{m}$  even the soft mode was almost completely gone.

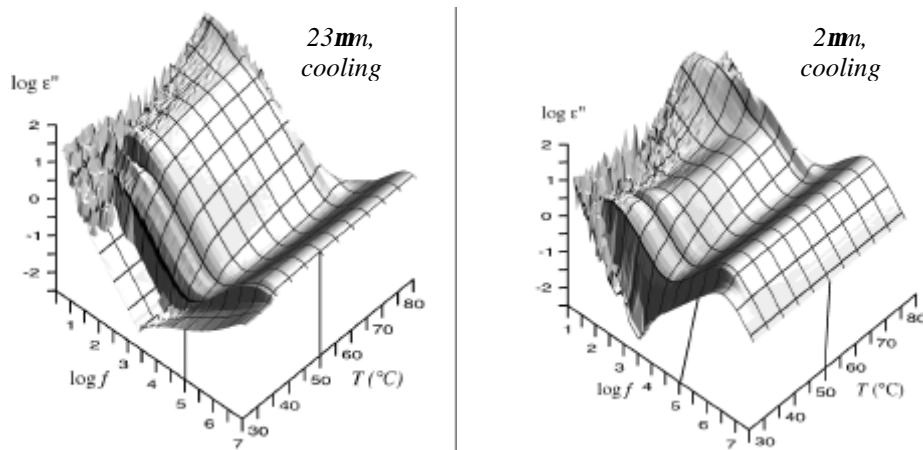


FIGURE 3 Dielectric spectra obtained on cooling in  $23\ \mu\text{m}$  (left) and  $2\ \mu\text{m}$  (right) cells with **CDMix5**.

*“Ferroelectric-Dopant” Mixtures*

As already reported in [8], **CDMix2** *i.e.* a “ferroelectric” dopant together with a host featuring both syn- and anticlinic phases, featured strong coexistence of  $\text{SmC}^*$  and  $\text{SmC}_A^*$  phases in the temperature region of the latter. In thick cells, the effect was mainly a supercooling effect as can be seen in the upper row of FIGURE 4, but the transition from  $\text{SmC}^*$  to  $\text{SmC}_A^*$  is very gradual, indicating a phase coexistence range of approximately 8 °C. In thin cells (lower row) the  $\text{SmC}^*$  phase was found to coexist with  $\text{SmC}_A^*$  also on heating. While it is thus difficult to say to which extent the two-phase state is thermodynamically stable in bulk, it is clear that the phase coexistence is stabilized by the presence of surface interactions.

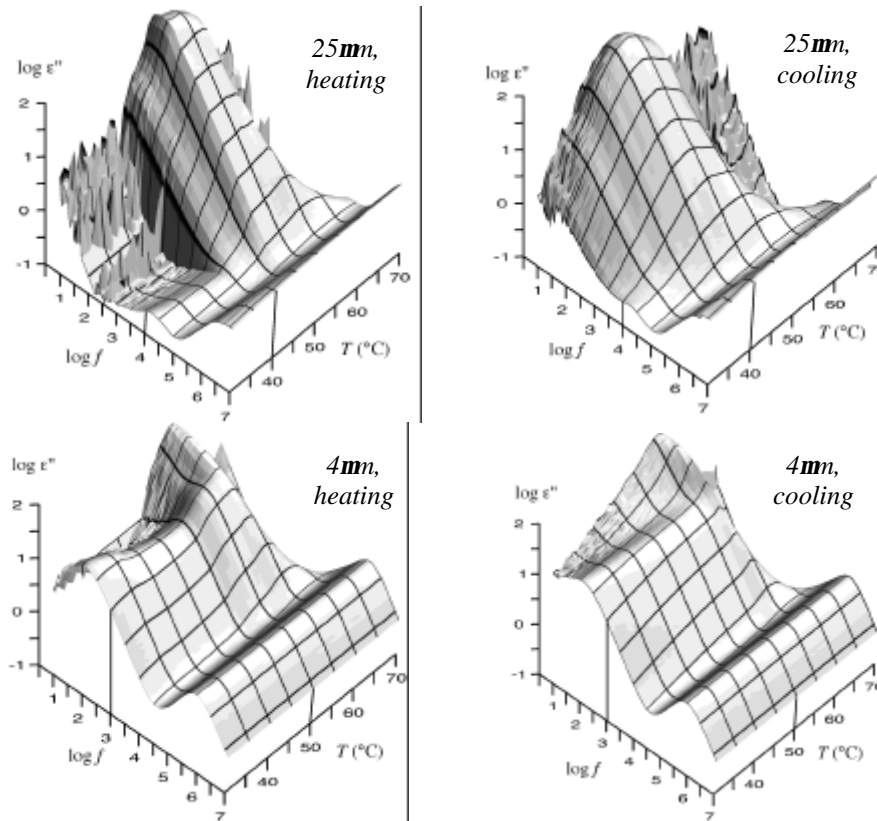


FIGURE 4 Dielectric spectra of **CDMix2** in thick (upper row) and thin (lower row) cells. A strong degree of  $\text{SmC}^*$  supercooling is seen in both cells. In the thin cell the  $\text{SmC}^*$  phase persists in the  $\text{SmC}_A^*$  temperature region also on heating.



## CHIRAL-DOPANT AFLC MIXTURES

In **CDMix4**, which is composed of the anticlinic host and the “ferroelectric” dopant, the phase sequence is clearly  $\text{SmA}^*-\text{SmC}_A^*$ , without any sign of coexistence with  $\text{SmC}^*$  in either cell. As in **CDMix3**, the dielectric response is very weak and can easily be completely quenched by applying a bias field.

The synclinic host together with the “ferroelectric” dopant (**CDMix6**) in principle shows a clear  $\text{SmA}^*-\text{SmC}^*$  phase sequence down to room temperature. However, in thin cells, and on heating in thick cells, the  $\text{SmC}^*$  phase azimuthal mode does not connect directly to the soft mode at the  $\text{SmA}^*-\text{SmC}^*$  transition. The short dip in absorption could possibly be a sign of an intermediate phase. As the other mixture, **CDMix6** is also very sensitive to the application of a DC-bias, making all the absorptions easy to quench. Another possible explanation for the absorption dip is that the measuring field itself is strong enough to switch the sample to the ferroelectric state in a narrow temperature interval, resulting in a non-existent azimuthal mode.

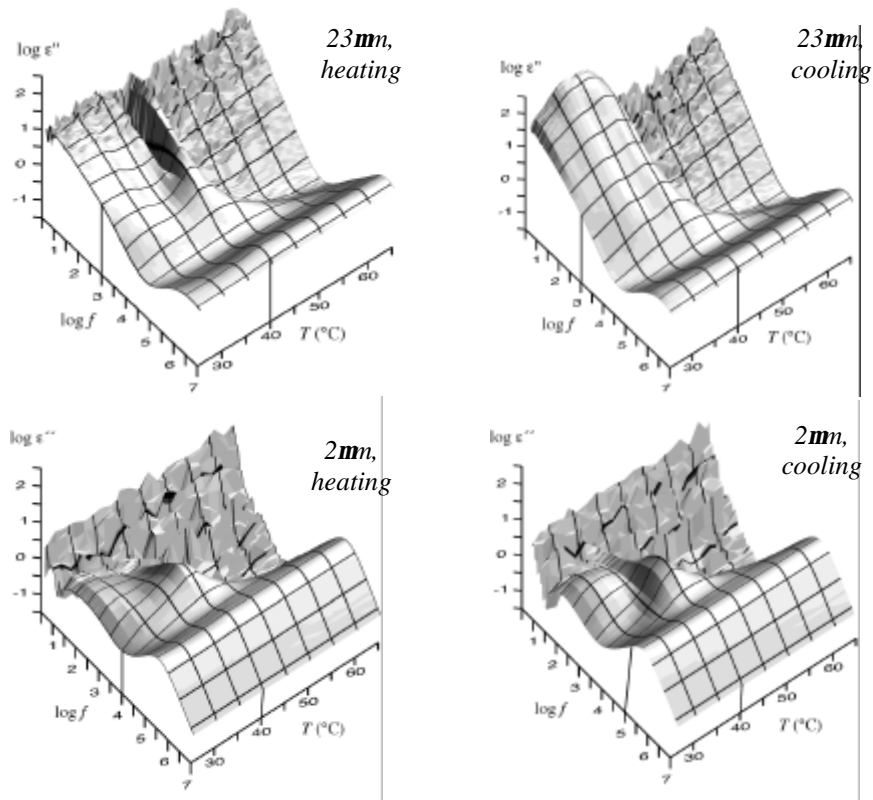


FIGURE 5 Dielectric spectra obtained in thick (upper row) and thin (lower row) cells on heating (left) and cooling (right) for **CDMix6**.

*Summary of Dielectric Spectroscopy Measurements*

The phase sequence of the mixture is mainly determined by the host. A strongly anticlinic host (**CDMix3** or **CDMix4**) does not permit a SmC\* phase, and a strongly synclinic host (**CDMix5** or **CDMix6**) does not permit a SmC<sub>A</sub>\* phase. A host with both structures gives a chiral mixture with both SmC\* and SmC<sub>A</sub>\* phases.

When using a host with both synclinic & anticlinic phases (**CDMix1** or **CDMix2**), coexistence between phases is sometimes observed. This is stronger in the mixture containing the “ferroelectric-like” dopant and in thin cells, which strengthens the hypothesis that surface influences promote the synclinic structure of the SmC\* phase over the anticlinic structure of the SmC<sub>A</sub>\* phase [13].

## CONCLUSIONS

A series of novel binary chiral-dopant mixtures have been prepared and their physical properties investigated using electrooptic and dielectric spectroscopy measurements. The phase sequence is mainly determined by the host, but the behaviour of mixtures possessing a SmC<sub>A</sub>\* phase may also depend very strongly on the type of dopant used. In certain mixtures, possessing both SmC\* and SmC<sub>A</sub>\* phases, coexistence between the two phases is observed. The degree and breadth of coexistence is strongly influenced by the type of dopant and the sample thickness; thinner cells appear to stabilize this coexistence by *extending* the SmC\* phase into the temperature region of the SmC<sub>A</sub>\* phase.

## References

- [1] N. A. Clark, S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
- [2] Y. Yamada, N. Yamamoto, K. Mori, N. Koshoubu, K. Nakamura, Y. Suzuki, *J. SID*, **1**, 289 (1993). A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, H. Takezoe, *J. Mater. Chem.*, **4**, 997 (1994).
- [3] J. Fuenfschilling, M. Schadt, *Proc. SID*, **31**, 119 (1990).
- [4] V. Pertuis, J. Patel, *Ferroelectrics*, **149**, 193 (1993).
- [5] S. Inui, N. Iimura, T. Suzuki, H. Iwane, K. Miyachi, Y. Takanishi, A. Fukuda, *J. Mater. Chem.*, **6**, 671 (1996).
- [6] T. Geelhaar, *Ferroelectrics*, **85**, 329 (1988).
- [7] C. J. Booth, D. A. Dunmur, J. W. Goodby, J. Haley, K. J. Toyne, *Liq. Cryst.*, **20**, 387 (1996).
- [8] D. D. Parghi, J. P. F. Lagerwall, G. Heppke, submitted to *Mol. Cryst. Liq. Cryst.*

## CHIRAL-DOPANT AFLC MIXTURES

- [9] H. Moritake, N. Shigeno, M. Ozaki, K. Yoshino, Liq. Cryst., **14**, 1283 (1993); J. Hatano, Y. Hanakai, H. Furue, H. Uehara, S. Saito, K. Murashiro, Ferroelectrics, **19**, 377 (1995).
- [10] L. K. M. Chan, G. W. Gray, D. Lacey, R. M. Scrowston, I. G. Shenouda and K. J. Toyne, Mol. Cryst. Liq. Cryst., **172**, 125 (1989).
- [11] A. D. L. Chandani, T. Hagiwara, Y- I. Suzuki, Y. Ouchi, H. Takezoe, A. Fukuda, Jpn. J. Appl. Phys., **27**, L729 (1988).
- [12] I. Nishiyama, J. W. Goodby, J. Mater. Chem., **3**, 149 (1993).
- [13] P. Rudquist, J. P. F. Lagerwall, M. Buivydas, F. Gouda, S. T. Lagerwall, N. A. Clark, J. E. Maclennan, R. F. Shao, D. A. Coleman, S. Bardon, T. Bellini, D. R. Link, G. Natale, M. A. Glaser, D. M. Walba, M. D. Wand, X. H. Chen, J. Mater. Chem., **9**, 1257 (1999).

### **Acknowledgements**

This work has been funded by the ORCHIS network and by the Swedish Foundation for Strategic Research.