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Anikó Vajda [a] , A. Tolochko [b] , G. Klimusheva [b] & S. Bugaychuk [b]

[a] Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Budapest, Hungary

[b] Institute of Physics of the National Academy of Sciences of Ukraine, Kiev, Ukraine

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Study of Structural Transition in Low-Temperature Ferroelectric Liquid Crystal Mixture

Anikó Vajda
Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Budapest, Hungary

A. Tolochko
G. Klimusheva
S. Bugaychuk
Institute of Physics of the National Academy of Sciences of Ukraine, Kiev, Ukraine

The structures as well as the SmA–SmC* transition of a ternary mixture that has ferroelectric phase in the range of room temperature have been investigated by means of both X-ray and optical microscopy methods. The low temperature ferroelectric mixture exhibits all typical spatial structural properties peculiar to layer-shrinking ferroelectric liquid crystal compounds.*

Keywords: low-temperature ferroelectric liquid crystal mixture; small angle X-ray scattering; spatial structure

INTRODUCTION

Ferroelectric or antiferroelectric liquid crystals and their mixtures are considered as perspective materials not only for wide range of display applications but also for systems of optical processing of signals and images, e.g., in high-quality electro-optical modulators, in electrically addressed and all-optical addressed devices. They can play significant role in real-time holography, optical computing, optical correlators,

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Address correspondence to Anikó Vajda, Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 49, Hungary. E-mail: vajda@szfki.hu

beam steering, focusing adaptive optics, and many others. For such implementations a LC modulator intends for selectively and precisely change the phase of laser light [1]. To find novel low-cost ferroelectric and antiferroelectric materials is of considerable interest for industrial applications. The expansion the area of potential applications is by improvement of physical performance of LC materials, but it is also important to extend a temperature dynamic range of a ferroelectric mesophase including the room temperatures.

All physical mechanisms in LC materials are closely associated with LC spatial structure and its changes caused by external environment. In the present paper we investigate the spatial structures of chiral LC mixture, which shows ferroelectirc behavior in the range near room temperature, by using the X-ray scattering technique. We determine changes both of the layer thickness and the tilt angle of molecules in the SmA*and SmC* phases. The obtained results can be used for further research of physical performances of this and similar low-temperature ferroelectric mixtures [2–4].

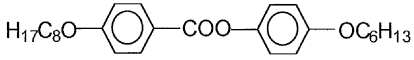
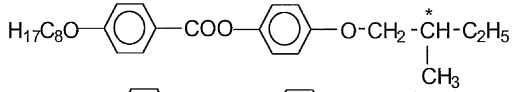
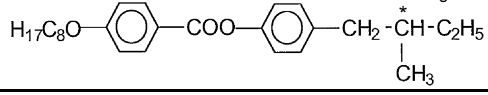
EXPERIMENTAL PART

Materials and Phase Diagrams

(S)-4-[2(methylbutyloxy)phenyl]-4′-n-(octyloxy)benzoate (Comp. 1), 4-(n-hexyloxy)phenyl-4′-n-(octyloxy)benzoate (Comp. 2) and (S)-4-[2(methylbutyl)phenyl]-4′-n-(octyloxy)benzoate (Comp.3) were used in preparation of binary and ternary mixtures. The phase transitions of the compounds investigated are summarized in Table 1.

The ferroelectric Comp. 1 exhibits monotropic SmC* mesophase below its SmA* and N* phases. Comp 2. is an achiral material showing

TABLE 1 Phase Transitions of Compounds Used for Mixtures

Compound	Structural formula	Phase transition (°C)
1		Cr 53 SmC 63 N 87 I
2		Cr 38 (37 SmC*) SmA* 54 N* 67 I
3		Cr 47.5 (42 N*) I

Monotropic phase in parantheses.

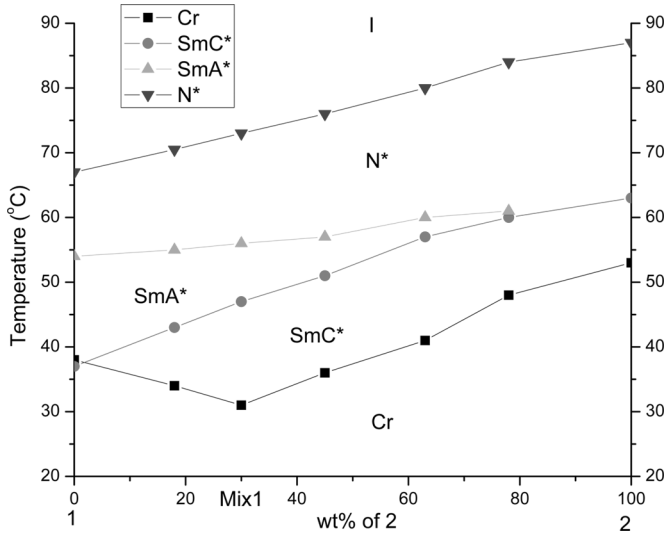


FIGURE 1 Phase diagram of binary systems.

enantiotropic SmC and N phases. Figure 1 depicts the phase diagram of binary mixtures of Comp. 1 and Comp. 2 (Table 2) exhibiting SmC*–SmA*–N* mesophase sequence.

The eutectic mixture Mix 1 was choosen for further investigations as a host material, to mix it with Comp. 3 as a guest, in order to decrease the melting points of the ternary mixtures and to extend the temperature range of SmC* phase. Figure 2 depicts a part of ternary phase diagram.

The ferroelectric phase of BW1 mixture was observable far below the room temperature, it was supercoolable down to -30°C. The concentration of the compounds and the phase sequence of the ternary mixture is shown in Figure 2.

Types of formed mesophases and phase transition temperatures were determined by polarizing microscopy. The samples were filled into unoriented sandwiched cells without any spacers. In Figure 3 both the broken fan shaped and the Schlieren textures of BW1 in SmC* phase appeared. Heating this sample the broken fan-shaped texture transformed into a fan-shaped, (Fig. 4) while the Sclieren area became homeotropic in the SmA* phase. Observations were made at magnification 90.

Heating further the sample the fan shaped area turned into a cholesteric fan shaped texture, while the homeotropic area transformed into a cholesteric Sclieren texture (Fig. 5).

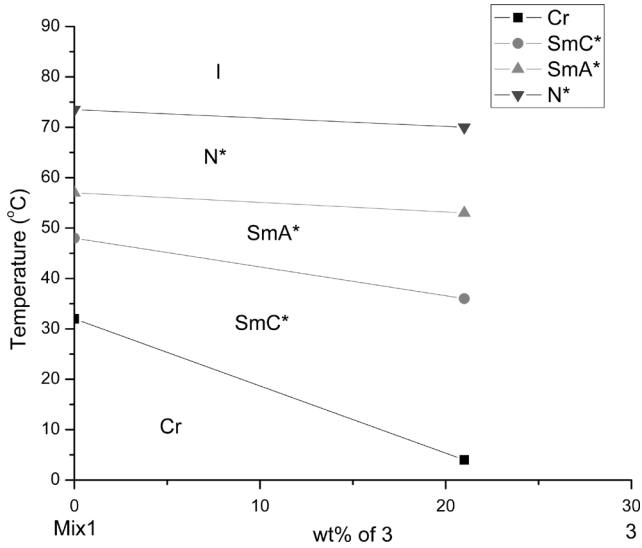


FIGURE 2 Phase diagrams of ternary systems.

X-ray Measurements

The technique of small angle X-ray diffraction is applied to study temperature structural properties of the ternary mixture BW1. The Cu Kα radiation of a 1.2 kW X-ray tube (Ni filtered) is used with further focusing through a slit. Non-aligned samples are prepared in a 0.7 mm Lindemann capillary tube, which is placed vertically inside a hot stage. The temperature of the samples is manually set with the temperature control ± 0.1°C. X-ray scattering patterns were collected at several temperatures from 20 up to 70°C while heating. The scattered radiation is analyzed with the help of a scintillation detector putting after a slit. The X-ray study includes the 2θ scans through a smectic layer peaks as well as diffuse reflections at wide angles.

TABLE 2 Phase Transitions of Mixtures

Mixture	Components	Phase transition (°C)
Mix. 1	1:2 = 70 wt%:30 wt%	Cr 32 SmC* 48 SmA* 57 N* 75 I
BW1	1:2:3 = 58 wt%:25 wt%:17 wt%	Cr 4 SmC* 36 SmA* 42 N* 70 I

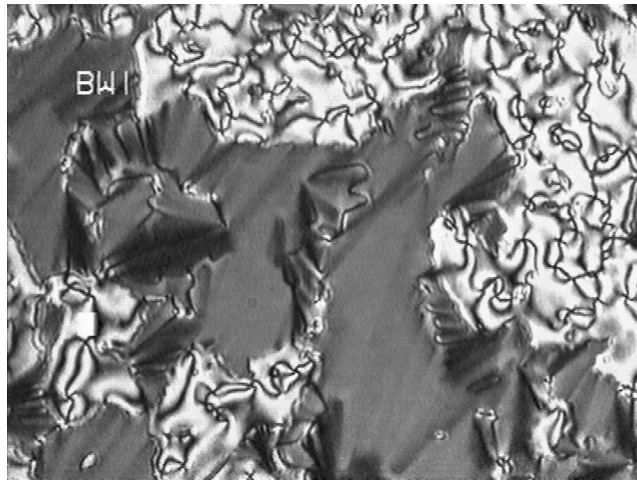


FIGURE 3 Texture of SmC*.

The experimental resolution is defined by the Gaussian function with 0.04° full width at half maximum along the scan direction. *PRIMUS*, which is a Windows PC-based system for small-angle scattering data analysis including programs *GNOM* and *PEACK*, was used [5]. The program *GNOM* provides a correction of instrumental distortions as well as it evaluates a distance distribution function.

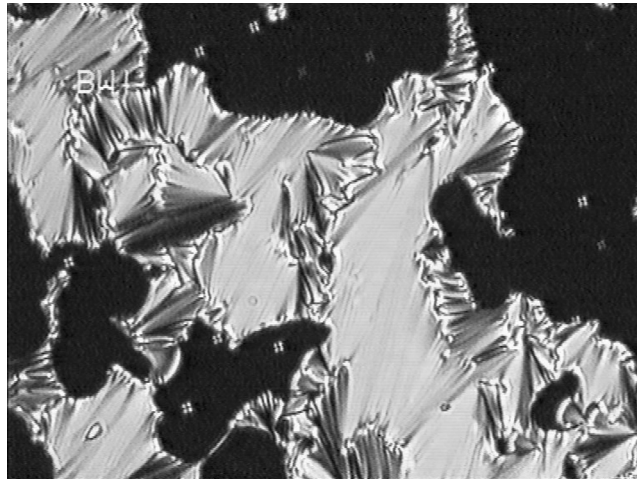


FIGURE 4 Texture of SmA*.

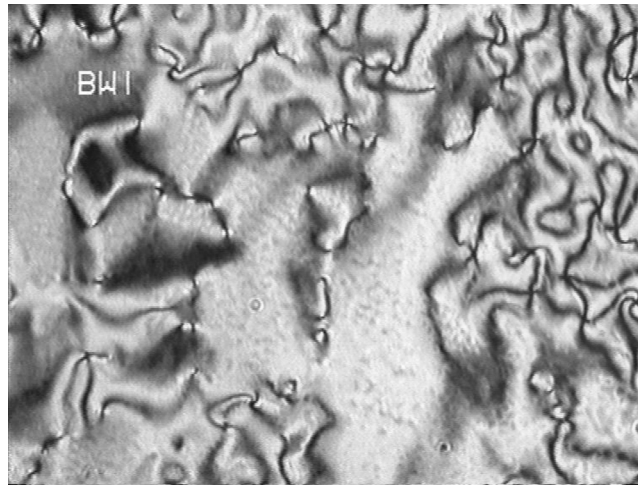


FIGURE 5 Texture of N*.

The program *PEACK* is designed to evaluate peak position in scattering profiles and to calculate the structural characteristics of the mesophases, such as Bragg spacing, a long range order dimension and a peak amplitude.

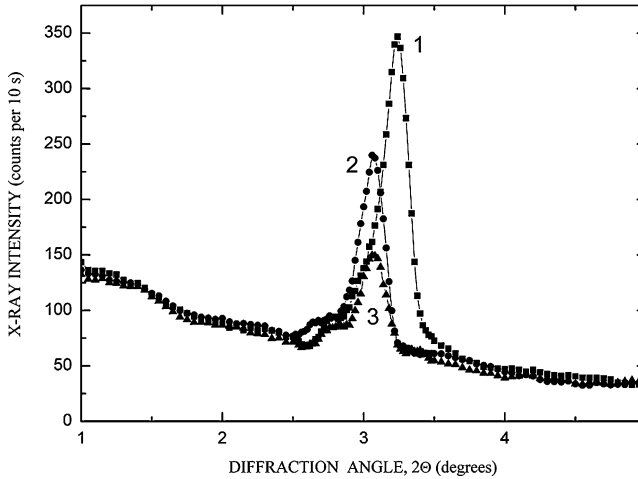


FIGURE 6 The temperature dependence of the small angle diffraction peak of the X-ray scattering for the mixture BW1. 1 – T = 20°C, SmC* phase; 2 – T = 46°C, SmA* phase; 3 – T = 54°C, N* phase.

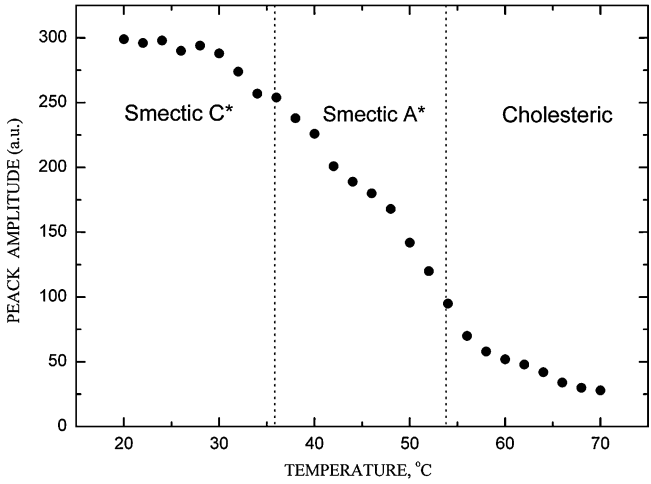


FIGURE 7 The peak amplitude *versus* the temperature for the mixture BW1.

The X-ray patterns of the mesophases both SmC* and SmA* show a sharp peak of a small angle reflection as well as a diffuse reflection at wide angles. The position of the small angle peak corresponds to the smectic layer spacing 27.4 Å for SmC* and 28.9 Å for SmA*.

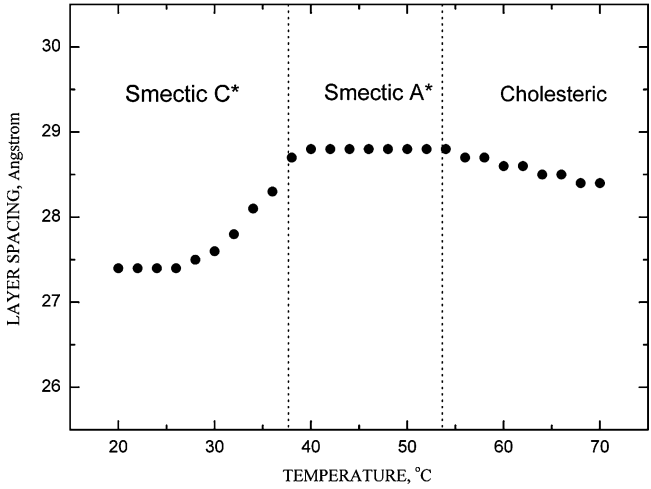


FIGURE 8 The temperature dependence of the layer spacing for the mixture BW1.

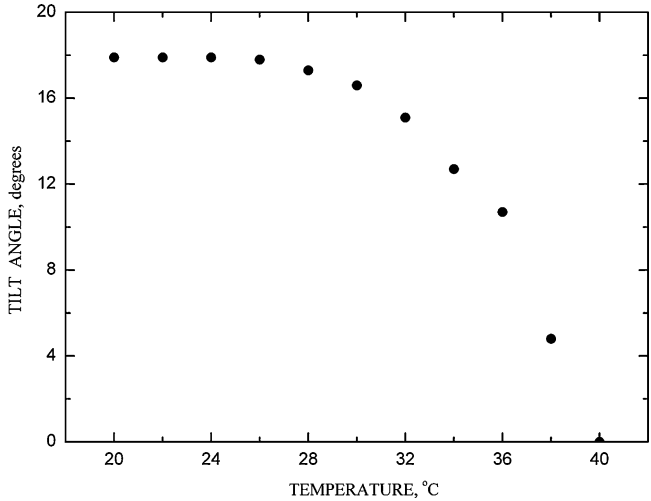


FIGURE 9 The temperature variation of the calculated tilt angle of molecules with respect to the layer normal for the mixture BW1.

The decrease of the peak amplitude through the transition from SmC* mesophase to the SmA* and N* phase is shown in Figure 7.

The wide angle diffuse reflection is associated with the separation distance between molecules within a layer that is determined around 4.5 Å, which is typical of the transverse intermolecular spacing.

To define properties of molecular ordering at the transition SmA*–SmC* we calculate the layer spacing and the tilt angle of molecules from small-angle X-ray scattering data as a function of temperature (Figs. 8 and 9). Please note, the layer spacing in the N* phase in the Figure 8 should be considered as the average intermolecular distance between the centers of molecules along their long axis.

The tilt angle and a layer thickness have a typical temperature behavior for the transition SmA* and SmC* phases [6], when the smectic layer spacing d is increasing and the tilt angle ϑ is decreasing in the SmC* phase on heating. The angle ϑ remains relatively small in SmC* mesophase, it is in the range about 18° (see Fig. 9).

This can serve as an evidence for the absence of important changes in the organization of the molecular packing in the phases under consideration. It is worth to mention, that the structural properties of the mixture BW1 are appeared both to heating and to cooling of the temperature. So it can be used as materials with high degree of reversibility.

CONCLUSION

From our obtained experimental data we thus conclude that a spatial packing of low-temperature mixture BW1 is typical for high-temperature ferroelectrics compounds with layer-shrinking SmA^*–SmC^* transition, but with small tilt angle in SmC^* mesophase. The considerable interest is in investigation and in comparison of similar both ternary and binary low-temperature ferroelectric mixtures in the aspect of study of "structure-property" relationship. The investigated mixture can be perspective for applications in electro-optical devices and in all-optical addressed devices with the addition of light absorbing dopants.

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