Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

High pressure studies on a binary mixture exhibiting two TGB phases

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To cite this Article Manjuladevi, V. and Madhusudana, N. V.(2005) 'High pressure studies on a binary mixture exhibiting two TGB phases', Liquid Crystals, 32: 8, 1071 — 1076

To link to this Article: DOI: 10.1080/02678290500291731

URL: http://dx.doi.org/10.1080/02678290500291731

Liquid Crystals, Vol. 32, No. 8, August 2005, 1071–1076

High pressure studies on a binary mixture exhibiting two TGB phases

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(*Received 1 March 2005; in final form 1 June 2005; accepted 2 July 2005*)

We report the pressure–temperature phase diagram of a binary mixture exhibiting two twist grain boundary phases. Our experiments show that both the TGB_A and $UTGB_C^*$ phases become bounded at elevated pressures in the mixture studied.

1. Introduction

In this paper we report the effect of elevated pressures on a binary mixture exhibiting twist grain boundary phases. The twist grain boundary (TGB) phase results from a competition between the smectic-like order and chiral interactions between appropriate molecules giving rise to a twisted structure. The intermediate phase is analogous to the vortex state in a type II superconductor under a strong magnetic field, as pointed out by de Gennes [1]. The detailed structure of the TGB_A phase was theoretically predicted by Renn and Lubensky [2]. It consists of a regular twisted arrangement of smectic A (SmA) blocks separated by grain boundaries made of arrays of screw dislocations. Goodby *et al.* [3] reported the first observation of the TGB_A phase in some highly chiral liquid crystals. Depending on the local smectic order two other types of TGB phases, viz. TGB_C and TGB_C^*, have also been theoretically described [4, 5]. The TGB_C phase has also been experimentally characterized [6].

Pramod *et al.* [7] in 1997 reported a new TGB phase called the undulating twist grain boundary C* ($UTGB_C^*$) phase with smectic C* (SmC*)-like block structure in a binary mixture of a chiral compound and a non-chiral compound. Several physical studies have been made to characterize this phase [7–10]. In planar aligned samples a square grid texture is observed [7, 8]. In homeotropically aligned cells the TGB_A phase is characterized by a filamentary texture, each filament corresponding to a rotation of the director by π radians, i.e. the width of the filament $=p/2$, where p is the pitch of the TGB helix. The filaments become undulated in the $UTGB_C^*$ phase with a periodicity which roughly corresponds to that of the square grid observed in the planar cells [7]. Observations on the meniscus region of free-standing films of the $UTGB_C^*$ phase using both transmission polarizing microscopy and fluorescence confocal polarizing microscopy also reveal that the filaments are undulated [9, 10]. Pramod *et al.* have proposed a structure for this phase which has twist deformation along all the three mutually orthogonal directions [7, 11]. More recently many single component systems exhibiting square grid textures [12–17] have been reported.

Few high pressure (HP) studies on systems exhibiting TGB phases are reported in the literature [18–21]. Carboni *et al.* [18] have reported the pressure–temperature (*P*–*T*) phase diagram of a pure compound exhibiting the phase sequence: isotropic (I)–TGB_A–SmC*. They found that the stability of the TGB_A phase is reduced at high pressures and the phase does not exist above ~250 bar. Anakkar *et al.* [19] have also found that in a pure compound exhibiting the phase sequence: I–blue phase (BP)–cholesteric (N*)–TGB_A–SmC*–Cr at atmospheric pressure, the TGB_A phase becomes bounded at elevated pressures.

Krishna Prasad *et al.* [20] have reported the concentration–temperature phase diagram of binary mixtures of two *chiral* compounds, viz. 4-(2- methylbutyl)phenyl 4′-*n*–octylbiphenyl-4-carboxylate (CE8) and 4-*n*-dodecyloxybiphenyl 4-(2-methylbutyl)benzoate (C12). In the binary mixture with 61 wt% of CE8 they found that the pressure–temperature lines of the N*–TGB_A and TGB_A–SmA phase transitions are collinear [20]. In a binary mixture with 25 wt% of CE8, they could induce the TGB_A phase at pressures above 460 bar [20].

Anakkar *et al.* [21] have carried out HP measurements on several compounds in the homologous series of 3-fluoro-4-(methyloxy)-4′-(4″-alkoxy-2″,3″-difluorobenzoyloxy)tolans ($nF_2BTFO_1M_7$) exhibiting TGB_A

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500291731

and TGB_C phases. They detected the phase transitions by thermobarometric analysis using an automated metabolometer. By comparing with the theoretical phase diagram predicted by Renn and Lubensky they identified the various phase transitions occurring at elevated pressures. They report that the slopes of SmC*–SmA, SmC*–TGB_A, SmC*–TGB_C and TGB_C–TGB_A transitions are negative, and that the SmC*–SmA, and SmC*–TGB_A transitions are of second order [19]. For such transitions the slope of the *P–T* diagram is given by $dP/dT=\Delta\alpha/\Delta\chi$, where $\Delta\alpha$ and $\Delta\chi$ are the jumps in the coefficient of thermal expansion and compressibility at the transition. They speculate that the negative slopes indicate a positive $\Delta\alpha$ and negative $\Delta\chi$ at the relevant transitions.

We have studied the *P–T* phase diagram of a binary mixture used by Pramod *et al.* [7]. The compound CE8 obtained from Merck does not exhibit the TGB_A phase, even though Wilson *et al.* [22] have reported that in a highly purified sample it exhibits the TGB_A phase with a range of ~0.5°C. The nematogen 4′-pentylbiphenyl-4-carboxylic acid 2-cyano-4-heptylphenyl ester, 7(CN)5, is known to exhibit smectic C-like short range ordering throughout the nematic range [23]. The binary mixture of 7(CN)5 with the chiral compound CE8 exhibits TGB phases in the concentration range 5–45 wt% of 7(CN)5. The temperature range of the TGB_A phase increases with increasing concentration of the non-chiral compound 7(CN)5. Above 34 wt% of 7(CN)5 the $UTGB_C^*$ phase is observed [7]. Apart from having sufficiently large chiral strength the system must have type II character to exhibit the TGB_A phase. Using electroclinic measurements in the SmA phase of these binary mixtures Dhara *et al.* [10] have demonstrated that the type II character becomes enhanced with increasing concentration of non-chiral component 7(CN)5. We have conducted high pressure measurements on a binary mixture with 36 wt% of 7(CN)5 (Mixt1), which exhibits both TGB_A and $UTGB_C^*$ phases at atmospheric pressure.

2. Experimental

The liquid crystal phase transitions were detected using a HP optical set-up. The sample temperature could be controlled to an accuracy of 25 mK. The sample was pressurized using a suitable oil by the priming action of a hand-pump. The line pressure was measured using a Bourdon type HEISE gauge [24]. The accuracy of pressure measurement was ~5 bar. The details of the HP set-up and the experimental method are discussed in detail elsewhere [24–26]. To trace the liquid crystal transitions, the transmitted intensities of aligned samples measured as functions of temperature at various fixed pressures were recorded. To take source intensity fluctuations into account, we use a lock-in amplifier (LIA; EG&G model 7260) in the dual reference mode. In this mode two different optical signals chopped at two different frequencies can be simultaneously measured using a single photodiode. A He-Ne laser (Oriel; 3 mW) beam of wavelength 633 nm is split into two beams using a beam splitter and allowed to pass through different windows of the same chopper (EG&G model 198) operating at frequencies in the ratio 11:18, with their sum frequency being fixed. These frequencies are chosen to be relative primes so that the mutual harmonic interference can be reduced significantly. The beam passing through the chopper window operating at 379 Hz passes through the sample placed between crossed polarizers which are mounted on rotatable graduated discs. The beam passing though the other window operating at 621 Hz is used as the reference beam. The two beams are combined at a beam combiner and detected using a single photodiode (Hamamatsu S1406, with a built-in amplifier) whose output is measured using LIA in the dual reference mode. The ratio of the intensity of the beam transmitted through the sample (I_{tr}) to that of the reference beam (I_{ref}) is used in the further processing of data.

In the optical measurements we use 5 mm thick (8 mm diameter) fused quartz cylinders which are optically isotropic. These are coated with polyimide and cured at 280°C for about an hour and then unidirectionally rubbed using soft tissue paper. The sample sandwich is prepared such that the directions of rubbing of the cylinders are parallel to each other, allowing the sample to align homogeneously with the director lying along the rubbing direction. A mylar spacer is used to fix the thickness of the sample. The main difficulty in the study of liquid crystals under high pressures is the isolation of the sample from the pressure transmitting medium. The sandwiched sample is snugly fitted into a fluran tube. An effective seal is realized by tightly binding thin steel wires around the tubing on both fused quartz windows (figure 1). The sample is mounted in the high pressure sample chamber along with other accessories [24]. Using an automated programme the profile of the ratio of transmitted intensity to reference intensity (I_{tr}/I_{ref}) along each isobar is recorded from the isotropic phase down to appropriate temperatures.

The compounds used in the study are: (i) 4-octyl-4′-cyanobiphenyl (8CB), (ii) 4′-butyl-4-heptylbicyclohexyl-4-carbonitrile (CCN47), (iii) Mixt1. CE8 was obtained from BDH Ltd; 7(CN)5 and CCN47 were obtained from Merck.

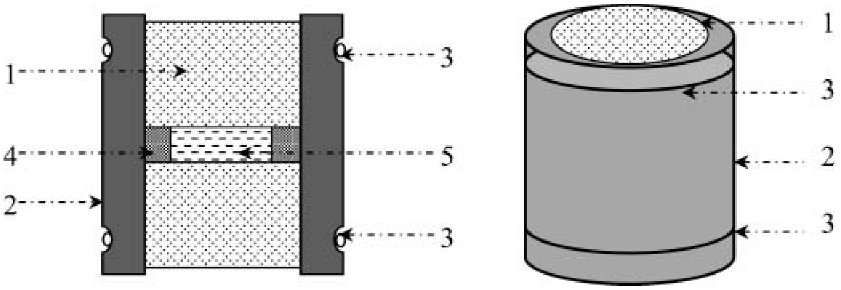

Figure 1. Schematic diagram of sample cell: 1-fused quartz window; 2-fluran tube; 3-steel wire; 4-Mylar spacer; 5-sample.

3. Results and discussion

3.1. *Pressure generation in the HP cell when a sample is mounted in a fluid state*

The method of mounting a sample, which is in a liquid crystalline phase at room temperature, in the HP cell is as follows. One of the pretreated fused quartz cylinders is snugly fitted in the fluran tube and a mylar spacer cut in the shape of a circular ring is placed on top of the fused quartz cylinder. The sample in the fluid form is filled into the circular gap of the mylar spacer. The other pretreated fused quartz cylinder is pressed from the top such that the sandwich of the two fused quartz cylinders is a snug fit in the fluran tube. Then as described in § 2, steel wires are wound on the fluran tube around both the fused quartz windows to isolate the sample from the pressure transmitting fluid. The sample is mounted in the HP set-up along with the other accessories [24].

We have carried out HP measurements on 8CB with the following phase transition sequence at atmospheric pressure: SmA$_d$–32.5°C–N–40°C–I. We observed that for a planar aligned sample mounted in the HP cell, even in the absence of any external pressure, the transitions occurred at higher temperatures: T_{SmAN} and T_{NI} were 38.2 and 46.5°C respectively. When an external pressure was applied, i.e line pressure of ~500 bar (as read by the Bourdan gauge) T_{NI} increased to about ~64.3°C. The $\mathrm{d}P/\mathrm{d}T_{\mathrm{NI}}$ value for 8CB has been measured earlier using various methods, viz. differential thermal analysis (DTA) [27], optical transmission [28], nuclear magnetic resonance (NMR) [29] and dielectric studies [30]. The reported values from all these studies are in agreement with each other and is ~29 bar K^{-1} [27–30]. Hence the application of an external pressure of ~500 bar is expected to change T_{NI} by ~17.5°C, and indeed it shifts by ~18°C as mentioned above. On releasing the external pressure, i.e. when the line pressure measured by the Bourdan gauge is 1 bar the T_{NI} was again found to be ~46.5°C. This shows that an excess pressure of ~185 bar is internally generated in the sample at this temperature. We have also carried out HP measurements on 8OCB, 4-cyano-4-hexyloxy-cyanobiphenyl (6OCB) and 4-cyanophenyl 4-*n*-heptyl-benzoate (CP7B), which are reported elsewhere [24–26]. These compounds were in the crystalline form when mounted in the HP sample chamber. For all these compounds, when the external pressure was 1 bar the phase transitions in the HP cell occurred at the transition temperatures of mesophases measured using the Mettler (FP 82) hot stage.

In the case of samples mounted in the HP cell by packing powdered crystals at room temperature, enough space is available for the sample volume to increase at the melting point. But in case of samples which are room temperature liquid crystals, the sample occupies the whole space including the gap between the fluran tube and the fused quartz cylinders by capillary action. As there is not enough space for the fluran tube to expand, the sample volume is fixed, and on heating the sample the pressure in the medium rises. Hence the transition temperatures also increase because of the internally generated pressure, even though externally no pressure has been applied to the sample. The effect obviously increases at higher temperatures. The inner and outer diameters of the fluran tube are 8 and 11 mm respectively. The external area per unit length is about twice that of the internal area of the fluran tube. Thus the external pressure is transmitted efficiently to the interior sample space, especially as the fluran tube can become compressed.

The compressibility of the medium is $\chi=-(1/V)(\mathrm{d}V/\mathrm{d}P)$ and the thermal expansion coefficient is $\alpha=(1/V)(\mathrm{d}V/\mathrm{d}T)$. For compensation of $|\Delta V/V|$, $\chi\Delta P=\alpha\Delta T$. For a typical mesogen the values of α and χ are $10\times10^{-4}\,\mathrm{K}^{-1}$ and $100\times10^{-12}\,\mathrm{cm}^2\,\mathrm{dyne}^{-1}$, respectively [31]. Assuming ΔT to be the temperature difference between the transition temperature and room temperature (the temperature at which the sample is mounted in the HP cell), the excess pressure ΔP can be estimated. At 46.5°C, i.e. the N–I transition point of 8CB in the cell, the estimated pressure ΔP ~200 bar which is in agreement with the value estimated above using the shift in N–I transition temperature. Therefore the *actual* pressure experienced by the room temperature liquid crystal mounted in the HP cell will be the sum of the internal pressure generated by the above process and the externally applied pressure measured by the Bourdan gauge.

The compound CCN47, with a large negative dielectric anisotropy, has the following phase transition sequence: Cr–28°C–SmA–30.6°C–N–59.7°C–I. This compound has a very low birefringence value, viz. $\Delta\mu$ $\sim$0.035 at 30°C [32]. As this compound is also in the liquid crystalline phase when mounted in the HP cell, both SmA–N and N–I transition temperatures are increased to $\sim$35.2 and 69.3°C, respectively, in the absence of external pressurization. The sample was subjected to an external pressure of up to $\sim$1.1 kbar, and the values of $\mathrm{d}P/\mathrm{d}T$ at the N–I and SmA–N transitions are $\sim$37 and 43 bar K^{-1}, respectively.

We also conducted HP experiments on a mixture of rod-like (8OCB) and banana-shaped molecules, which was found to exhibit a uniaxial SmA to biaxial SmA ($\mathrm{SmA_b}$) transition [33]. This sample was in the $\mathrm{SmA_b}$ phase at room temperature, and the $\mathrm{SmA_b}$–SmA transition point shifted by $\sim$16.6°C without any external pressurization. From the $\mathrm{d}P/\mathrm{d}T$ values measured at high external pressures, the estimated internally generated pressure is $\sim$700 bar in the smectic phase, which is very large in comparison with those observed for the other samples discussed earlier. One possible reason may be that the compressibility in the smectic phase of the mixture may be significantly smaller than that in the nematic phase. The measured $\mathrm{d}P/\mathrm{d}T$ values are $\sim$46 and 52 bar K^{-1} for the SmA–N and $\mathrm{SmA_b}$–SmA transitions, respectively.

3.2. *P–T phase diagram of a binary mixture exhibiting twist grain boundary phases*

We carried out HP measurements on a binary mixture of CE8 with 7(CN)5 (Mixt1). CE8 exhibits the following phase transitions: I–BP–SmA–SmC*–smectic I* (SmI*). Shankar Rao *et al.* [34] conducted HP measurements on CE8 and found that the temperature ranges of the SmA and SmI* phases increase with increasing pressure, while that of the SmC* phase decreases with increase in pressure. The slopes of all the transitions are positive in the *P–T* plane.

Mixt1 exhibits the following phase transition sequence at atmospheric pressure: I–121.6°C–N*–78.6°C–$\mathrm{TGB_A}$–63°C–$\mathrm{UTGB_C}$*–59.3°C–SmC*. This sample was in the crystalline phase when mounted in the HP cell. The fused quartz windows were treated for planar alignment. We carried out the measurement of the optical intensity of a sample of Mixt1 by placing it between crossed polarizers for detecting the phase transition temperatures at various pressures. The data at atmospheric pressure (which agree with the values given above), as well as at a pressure of $\sim$470 bar, are shown in figure 2. Even though the data is somewhat noisy, as the phase transitions were also detected by observing the textural changes in the sample using a specially fitted microscope, we could trace the transition points. The sudden change in the transmitted intensities corresponding to phase transitions are indicated by arrows.

The *P–T* phase diagram of Mixt1 is shown in figure 3. The value of $\mathrm{d}P/\mathrm{d}T_{\mathrm{N^*I}}$ $\sim$26.6 bar K^{-1} is comparable to that of pure CE8 [35]. The $\mathrm{TGB_A}$ phase becomes bounded at a pressure $\sim$900 bar. This behaviour is similar to that observed by Carboni *et al.* [18] and Anakkar *et al.* [21] in pure component systems. The $\mathrm{UTGB_C^*}$ phase also becomes bounded, at an even lower pressure of $\sim$600 bar. For the $\mathrm{TGB_A}$ phase to form, the Landau–Ginzburg parameter $\kappa=\lambda/\xi$ must satisfy $\kappa>2^{-1/2}$, where λ is the penetration depth for twist deformation and ξ is the smectic order parameter coherence length [35]. The disappearance of the TGB phases at high pressures probably indicates that the Ginzburg parameter κ decreases with increasing pressure in the system studied [18].

The slopes of all the three transitions, viz. N*–$\mathrm{TGB_A}$, $\mathrm{TGB_A}-\mathrm{UTGB_C^*}$ and $\mathrm{UTGB_C^*}$–SmC* (figure 3) for Mixt1 are positive, unlike in the systems studied by Anakkar *et al.* In the phase diagrams reported by Anakkar *et al.* [21], for the homologue with $n=9$ the $\mathrm{TGB_A}$ phase becomes bounded at elevated pressures. On the other hand, for the higher homologues with $n=10$ to 12 the thermal range of TGB phases increases with increasing pressure. In homologues with $n=14$ and 16, TGB phases are induced at high pressures. The system Mixt1 is a binary mixture of compounds with relatively short alkyl chains; CE8 has an aliphatic chain of 8 carbon atoms and 7(CN)5 has on each end aliphatic chains of 7 and 5 carbon atoms, respectively. The disappearance of TGB phases at elevated pressures in Mixt1 is thus analogous to the trends seen in the lower homologues by Anakkar *et al.*

4. Conclusions

We have found that an excess pressure is generated when a sample in the fluid state is mounted in our high pressure cell, as the fluran tube cannot expand. On the other hand, an external high pressure is transmitted well to the interior of the sample, implying that the tube can be compressed. We have presented the *P–T* phase diagram of a binary mixture exhibiting two TGB phases, both of which become bounded at elevated pressures.

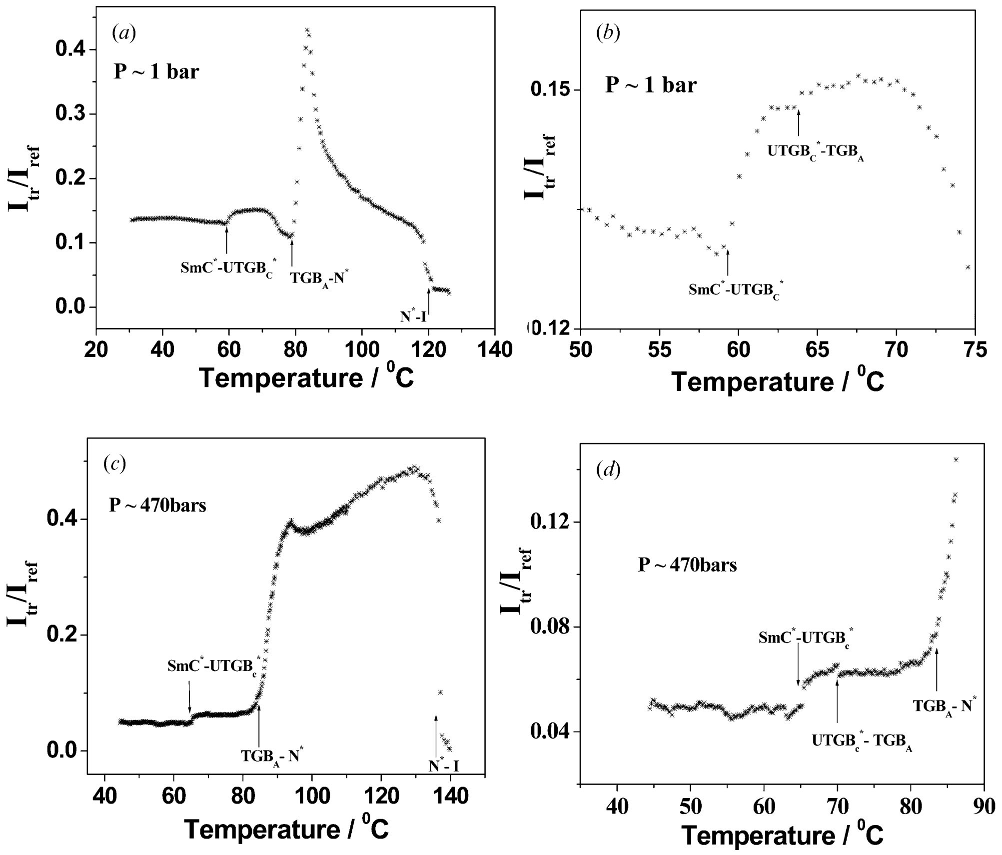

Figure 2. The temperature variation of the ratio of transmitted intensity to reference intensity from a sample of Mixt1 enclosed between fused quartz cylinders treated for planar alignment at atmospheric pressure, as well as at ~470 bar: (*a*) and (*c*) over the entire temperature range, (*b*) and (*d*) over a narrow range of temperatures around the mesophase transitions involving TGB phases.

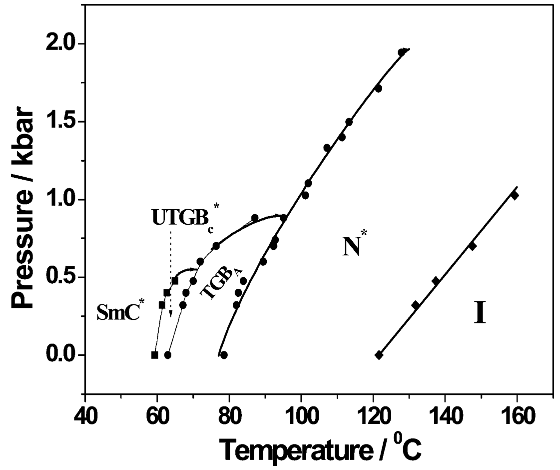

Figure 3. The pressure–temperature phase diagram of Mixt1.

Acknowledgements

We would like to acknowledge Dr R. Pratibha for discussions and Mr M. Mani for technical assistance.

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