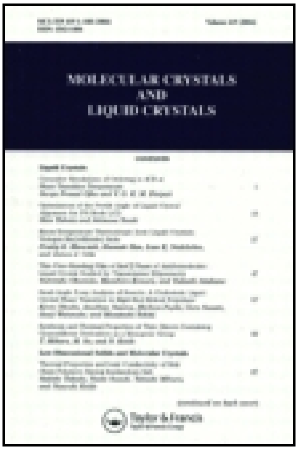

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ELECTRICAL PROPERTIES OF DOMAIN BOUNDARY IN PHOTOCONDUCTIVE SMECTIC MESOPHASES AND THEIR CRYSTAL PHASES

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Electrical Properties of Domain Boundary in Photoconductive Smectic Mesophases and their Crystal Phases

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We have investigated the charge transport properties in smectic photoconductive liquid crystal of 2-phenylnaphthalene derivatives in focus on the electrical nature of the boundaries at the phase transition from liquid crystalline phase into the crystal phase. With systematic studies of charge transport and collection by transient photocurrent measurements and molecular alignment by X-ray diffraction at the phase transition, it was revealed that the defective nature of the crystalline boundaries takes the shape of shallow traps at the initial stage and of deep traps successively, and finally the polydomain allowance for the carrier transport in mesophases disappears completely when the phase transition takes place into the crystalline phases.

Keywords: smectic mesophase; photoconductivity; carrier transport; poly domain; phase transition

INTRODUCTION

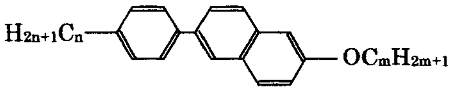
In order to relax the present limitation of the organic photoconductors in device application, a new material exhibiting a high mobility independent of electric field and temperature and little deep defect density has to be realized. From this viewpoint, we had paid our attention to the liquid crystalline materials that have enhanced carrier transport property due to their self-organized molecular alignment. We found that the calamitic, i.e., rod-like liquid crystals exhibit the fast electronic carrier transport [1-4] comparable to the discotic ones [5]. 2-phenylnaphthalene derivatives are typical examples, whose smectic mesophases exhibit unique features in carrier transport, i.e., a fast hole or electron mobility up to 10^{-2} cm^2/Vs and its independence of temperature and electric field. In addition to these facts, the carrier transport is not degraded even in polydomain [6]. It is likely that these superior carrier transport properties are attributed to no discontinuity of molecular alignment in a short range originated from the fluid nature of liquid crystals. As demonstrated with the excellent single-domain-like carrier transport in polydomain and fast mobility up to 10^{-2} cm^2/Vs independent of electric field and temperature, it is concluded that the liquid crystalline photoconductors have a high potential to relax the present limitation of the conventional organic photoconductors in device application.

According to the current study up to now, higher carrier mobility is obtained in more highly ordered mesophases. Then, there are two questions we are interested in: How fast the carrier mobility can speed up in highly ordered mesophase? Is there the essential difference of carrier transport properties between the mesophase and the crystal? We can learn the answer of these questions with reference to the carrier mobility of own single crystal. Thus, we have investigated the carrier transport properties in 2-phenylnaphthlene derivatives in focus on its change before and after the phase transition from the mesophase into the crystalline phase in detail.

EXPERIMENTAL

Material

We used two photoconductive smectic liquid crystals, 2-(4'-octylphenyl)-6-dodecyloxynaphthalene (8-PNP-O12; K 79°C SmB 101°C SmA 128°C Iso) and 2-(4'-octylphenyl)-6-butyloxynaphthalene (8-PNP-O4; K 50°C SmE 123 °C SmA 128°C Iso), which exhibit different mesophase, i.e., SmB and SmE phases prior to crystallization on cooling. These materials were synthesized as described elsewhere [5], and purified with recrystalization from n-hexane. The purified samples were capillary-filled into the cells at isotropic phase, which consisted of two ITO electrodes spaced by polyimide film spacer (25-100 μm). We did not use any alignment technique for preparing liquid crystal cells so as to enhance the defect formation in the bulk and at the boundary, in order to exclude experimental ambiguity. By changing the cooling rate from isotropic phase to mesophase, we controlled the domain size of smectic texture in a range of 10 -100 μm.



n=8, m=12 : 8-PNP-O12
n=8, m=4 : 8-PNP-O4

Figure 1. Chemical structure of phenylnaphthalene derivatives

Evaluation of Carrier Transport Properties

For characterization of carrier transport properties, the time-of-flight (TOF) measurement [7] was used. In the TOF measurement, the liquid crystal cell was fixed on a hot stage whose temperature was controlled within accuracy of 0.1K. Photoexcitation in main absorption band of the liquid crystals was carried out with beam-expanded N_2 pulse laser (λ = 337nm, pulse width = 600ps, maximum energy of Photoexcitation = 65μJ, illuminated area on sample = 10mm square), which is controlled by the external trigger with an appropriate interval in order to acquire consequential data of desired temperature profile without after effect of the excitation. One carrier condition was well established because of a sufficiently short penetration depth of the illuminated light of 337 nm in the sample cell compared with the cell thickness over several tens μm. Transient photocurrent under programmed step voltages generated by Keithley 237 high voltage source measure unit was recorded by a digital storage oscilloscope (Nicolet Pro92). The electric fields applied to the cells were fixed in order to simplify the discussion. We determined the transit time as an inflection point in a double logarithmic plot of the obtained transient photocurrent as a function of time. We measured the transient photocurrents at different temperatures and determined the carrier mobility. Simultaneously, the collected charge at each photoexcitation was calculated by integration of the transient photocurrent with the time at each temperature. In order to detect the formation of domain boundaries or phase transition during the measurement, He-Ne Laser beam was introduced across the cell through a small hole in the hot stage, which enabled us to recognize phase transition in the cell from dispersed optical pattern projected behind the hot stage.

X-Ray Diffraction

The fast carrier transport property of calamitic liquid crystalline photoconductors is thought to be short molecular distance in closely packed liquid crystalline molecules in smectic layers which results in the effective overlap of their molecular orbital. From this point of view, the X-ray diffraction study was carried out by X-ray diffractometer (Rigaku RINT-1500) as a function of the temperature in order to get the information about the change in the molecular distance and orientation in accordance with the phase transition.

RESULTS AND DISCUSSIONS

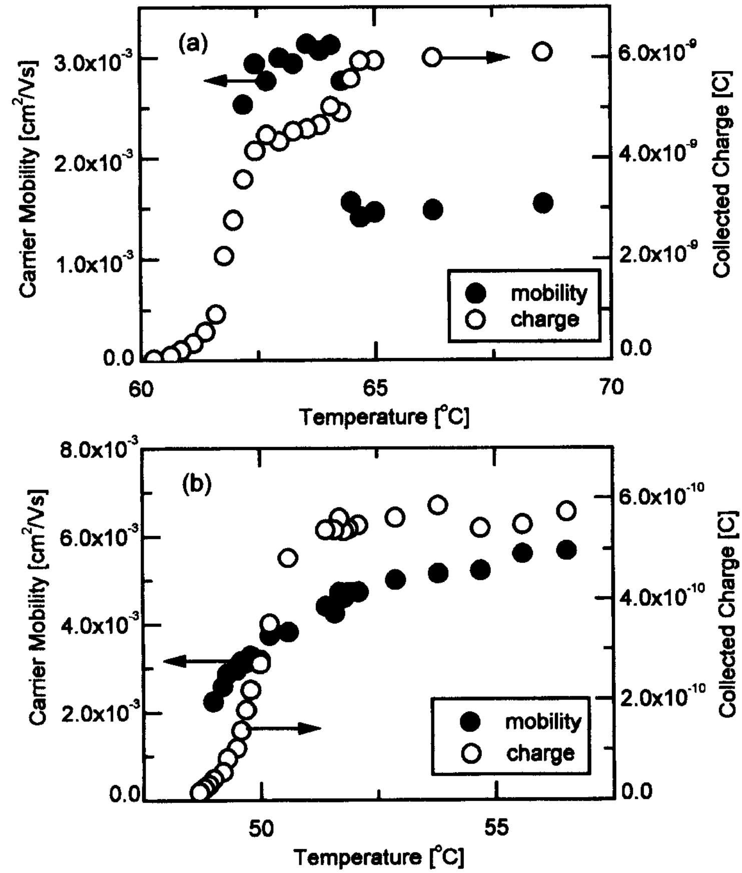


Figure.2 Temperature dependence of carrier mobility and amount of collected charge for (a) 8PNPO12 and (b) 8PNPO4 between ITO//ITO cells. Cell gap and applied voltage were fixed to 50mm and 500V, respectively.

Through the TOF measurement, carrier transport and charge collection characteristics were investigated around the transition temperatures for SmB-Crystal phase of 8-PNP-O12 and for SmE-Crystal phase of 8-PNP-O14 in detail. Results are shown in Figure 2. The amount of collected charges started to decrease just after transition to crystalline phase while cooling the cells. Behavior of phase transition could confirm with the projected pattern of He-Ne laser beam across the cell. Basically, carrier mobility is independent of temperature in smectic mesophase.

At the early stage after the phase transition to crystal the carrier mobility started to drop slightly with decreasing temperature in both of the liquid crystalline materials, although an abrupt increase of the mobility at a short temperature range went ahead in 8-PNP-O12. This indicates the crystalline boundaries formed take the shape of shallow traps, resulting in the reduction of the mobility. Interestingly, there was a clear difference in the charge transport behavior of 8-PNP-O12 and 8-PNP-O4 after the transition: with further cooling down the cell temperature, the mobility of 8-PNP-O12 abruptly dropped and no more transit was recognized in transient photocurrent, while the mobility gradually decayed in 8-PNP-O4. On the other hand, the charge collection exhibited a similar result as a function of temperature: the collected amount of photo-induced charges was rapidly reduced in a range of 5 K after the phase transition to the crystalline phase irrespective of the mesophases prior to the crystallization, SmE phase in 8-PNP-O4 and SmB phase in 8-PNP-O12. Finally, the carrier transport in bulk completely vanished, indicating the formation of deep traps in the cell. It is reasonable that the deep defect formation is attributed to the electrically active gain boundaries in accompany with the polycrystal formation.

To understand how the present difference in carrier transport decay after the phase transition to the crystalline phase in 8-PNP-O12 and 8-PNP-O4 comes, we looked at X-ray diffraction pattern at a temperature range around SmX-K transition temperature. The results are plotted in Figure 3. In case of 8-PNP-O12, it is obvious that molecular packing drastically changed with the SmX-K transition, while it is not the case of 8-PNP-O4. When the drastic change in molecular packing

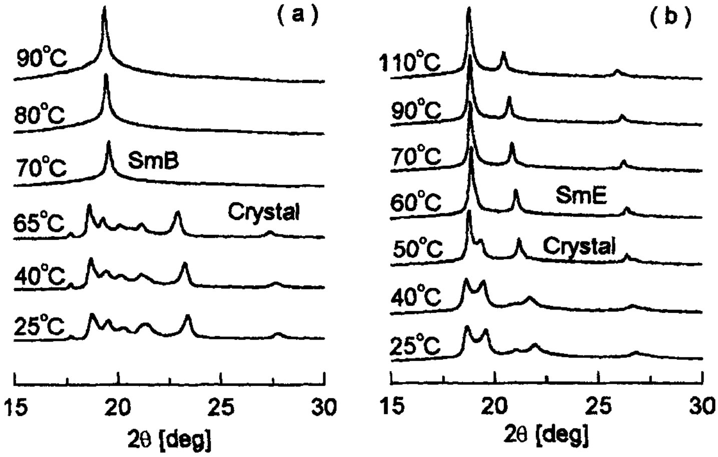


Figure. 3. Temperature dependence of X-Ray diffraction pattern of (a) 8-PNP-O12, (b) 8-PNP-O4.

occurs in crystalline phase, structural relaxation is needed to release accumulated strain because the fluidity no longer exists. Such the event of "structural collapse" in the boundaries can explain that the carrier transport abruptly vanishes due to the deep defect formation. That is the case of 8-PNP-O12 in accordance with the transition to the crystalline pahse. It is plausible that the structural similarity of the molecular alignment between the crystalline and liquid crystalline phases retards the collapse in 8-PNP-O4. Alternative explanation is that the super-cooling mesophase may formed just after the transition in 8-PNP-O12, although no obvious pattern that indicates a new mesophase mesophase observed.

CONCLUSION

The electrical nature of the boundaries formed in the phase transition from liquid crystalline phase into the crystal phase in two 2-phenylnaphthalen derivatives was investigated by measuring transient photocurrents at around the phase transition temperature. Formation of charge carrier traps in crystalline phase, i.e., shallow traps at the early stage of the transition and deep traps thereafter, was observed, resulting in the reduction of the mobility and the carrier distinction, respectively. It is found that the discontinuity in molecular alignment around the phase transition temperature from the liquid crystalline phase to the crystalline phase observed from X-ray diffraction pattern is responsible for the collapse of the charge transport properties. Thus, the mesophase aside to crystalline phase influence the formation of traps at the phase transition, resulting in degradation of the carrier transport property in crystalline phase.

In conclusion, the structure sensitive defect formation at the phase transition to crystalline phase support the idea that the fluidity of the mesophase relax the accumulated strain at the phase transition and results in electrical inactive domain boundaries in the mesophase.

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