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Liquid Crystals

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Makoto Yoneya[a,b]; Shintarou Takada[c]; Yoji Maeda[a]; Hiroshi Yokoyama[a,b]
[a] Liquid Crystal Nano-System Project, ERATO/SORST, Japan Science and Technology Agency, 5-9-9 Tokodai, Tsukuba 300-2635, Japan [b] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8568, Japan [c] Materials Research Laboratory, Hitachi, Ltd., 7-1-1 Omika, Hitachi 319-1292

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Electro-optic response of cubic liquid crystal compounds in Kerr cell geometry

Makoto Yoneya[a,b]*, Shintarou Takada[c], Yoji Maeda[a] and Hiroshi Yokoyama[a,b]

[a]*Liquid Crystal Nano-System Project, ERATO/SORST, Japan Science and Technology Agency, 5-9-9 Tokodai, Tsukuba 300-2635, Japan;* [b]*Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba 305-8568, Japan;* [c]*Materials Research Laboratory, Hitachi, Ltd., 7-1-1 Omika, Hitachi 319–1292*

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We present the results of our investigations on the electro-optic response of the cubic phase liquid crystal compounds 1,2-bis-[4-n-octyloxy-benzoyl]-hydrazine (BABH8) and 4'-n-hexadecyloxy-3'-nitrobiphenyl-4-carboxylic acid (ANBC16) in Kerr cell geometry. The AC electric field response in the BABH8 cubic phase was found to be as small as that of the isotropic phase, even though there was a response in the adjacent smectic C (SmC) phase. The response in the SmC phase means that the BABH8 molecule itself has an electric field coupling ability, but this ability is strongly inactivated in the cubic phase. This inactivity to the AC fields was also found in the cubic phase of ANBC16. This behaviour could be explained by the small structural unit size of the cubic phase.

Keywords: Kerr effects; blue phase; optical isotropy; birfringence

1. Introduction

Liquid crystal (LC) materials that spontaneously form three-dimensional (3-D) structured mesophases, such as blue phases (BPs), have attracted increasing interest due to their emerging applications in, for example, 3-D BP lasers (*1*). A display application has also been discussed which eliminates the need for surface LC alignment treatment (a rubbing process) by adapting the self-assembling property of BPs to form an optically isotropic structure (*2*). Electric field-induced birefringence, e.g. the Kerr effect, is then used to control the display transmittance. However, the very narrow temperature range (only a few degrees Celsius) of BP formation limits the applications, although expansions of this range with novel materials have recently been reported (*3, 4*).

The cubic (Cub) phase is yet another 3-D structured LC phase which also exhibits optical isotropy, and its temperature ranges are several tens of degrees wide. To apply BPs for displays, we should make the pitch of the LC material sufficiently small to avoid the Bragg diffraction in a visible wavelength region (*5*). In the Cub phase, such control is not necessary since its structural periodicity is already sufficiently small (around 10 nm). Therefore the Cub phase also has the potential for application to rubbingless Kerr effect displays (*6*). However, as far as we know there have been no field response studies in the Kerr cell geometry of the Cub phase, although the field-induced smectic C (SmC) to Cub phase transitions in indium–tin–oxide (ITO) sandwich cells have been studied (*7*).

In this paper, we report the electro-optic response measurements of Cub phase compounds 1,2-bis-[4-n-octyloxy-benzoyl]-hydrazine (BABH8) and 4'-n-hexadecyloxy-3'-nitrobiphenyl-4-carboxylic acid (ANBC16) in Kerr cell geometry to clarify the potential for applications and also the difference between BPs.

2. Experimental

BABH8 was prepared according to the method of Schubert et al. (*8*). BABH8 has the phase sequence of crystal 140.8°C Cub 158.4°C SmC 162.3°C isotropic phases (*9*). The sample was inserted into the cell with a cell gap of d=50, 12, 2.4 µm (maintained by a film spacer) in the isotropic liquid state. The cell configuration was the same as in the Kerr effect study of polymer-stabilised BP materials (*2*), i.e. the comb-type interdigitated electrodes were on only one side of the glass substrate. The comb electrodes were chrome with a width of 7.5 µm and their adjacent separation was 17.5 µm. The cell substrate surfaces were clean glass surfaces prepared without any alignment layers or rubbing treatment. The cells were placed in a Mettler FP82 hot stage to which an AC electric field (with a frequency of 0.1–10 kHz and strength E up to $7\,\mathrm{V\,\mu m^{-1}}$) was applied. The influence of the AC electric field application was examined with a polarising optical microscope (POM, Nikon Optiphoto T2-TOL) and the transmission of the cell was measured with a photodetector (Nikon Photometry System: P100 and P102).

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*Corresponding author. Email: makoto-yoneya@aist.go.jp

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3. Results

Figure 1 shows the AC (at 1 kHz) electric field-induced transmittance variations of the cell in the SmC phase at 153°C and the Cub phase at 140°C (in our samples, the transition temperatures were a slightly shifted from the reported values (*9*), probably due to the cell confinement effects). The transmittance variations in the Cub phase fluctuated around 0.0025% and may have been close to the noise level of the measurement. Corresponding variations in the SmC phase look small but there was a field-induced response as in the POM images inserted in Figure 1. In this case, crossed polarisers were set with their axis at ±45° to the comb electrodes, i.e. to the direction of the applied electric field. The transmittance variations in the SmC phase were enlarged when changing the directions of the crossed polariser axis and with a smaller cell gap $d=2.4\,\mu\mathrm{m}$, as shown in Figure 2. In the Cub phase, however, the variations were still at the noise level and the POM image looks completely dark over the whole cell irrespective of the directions of polariser axis. Measurements were taken at different frequencies of the AC field from 0.1 to 10 kHz, but the response was basically the same except for the occurrence of a very small field-sign-dependent response in the Cub phase at very low frequencies below 1 Hz. The response was observed as alternative light leakage around only one of the pairs of comb electrodes (sign-dependent) and was almost certainly caused by some ion impurities.

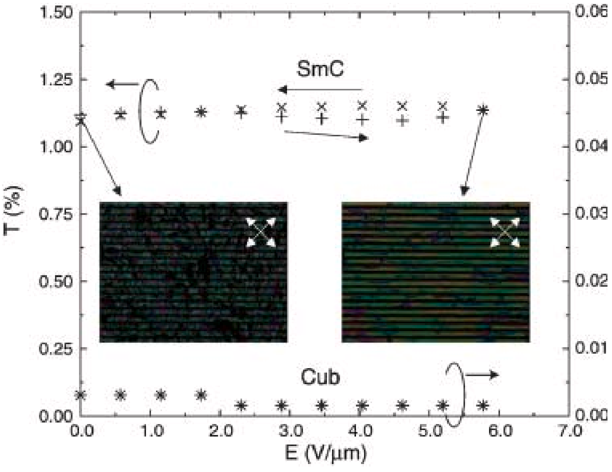

Figure 1. Electric field-induced transmittance variations of BABH8 in the cell with $d=12\,\mu\mathrm{m}$: SmC phase at 153°C (+ for increasing and × for decreasing electric fields), Cub phase at 140°C (*, 25 times enlarged on the vertical scale). Insert: POM images of BABH8 SmC phase without electric field (left) and with $E=5.7\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ (right), horizontal black stripes and white arrows correspond to the chrome comb electrodes and the polariser directions, respectively.

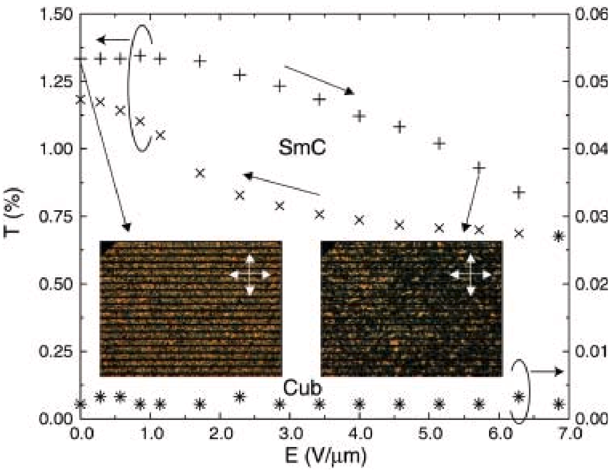

Figure 2. Electric field-induced transmittance variations of BABH8 in the cell with $d=2.4\,\mu\mathrm{m}$: SmC phase at 156°C (+ and ×), Cub phase at 140°C (*).

To detect the response in the Cub phase, we also measured the field-induced phase variations with the custom-made transmittance mode ellipsometry (ITO transparent comb electrodes were used in the measurements). The results in Figure 3 show that the response in the Cub phase was as small as that in the deep isotropic phase (10°C higher than the transition temperature).

These results show that we can achieve a uniform black state without any surface treatment, but there is only a negligible electric field response in the BABH8 Cub phase. The AC field response in the SmC phase means that the BABH8 molecule itself has electric field coupling ability, which may be due to dielectric anisotropy, but this ability is strongly inactivated in the Cub phase. To check this lack of electric field

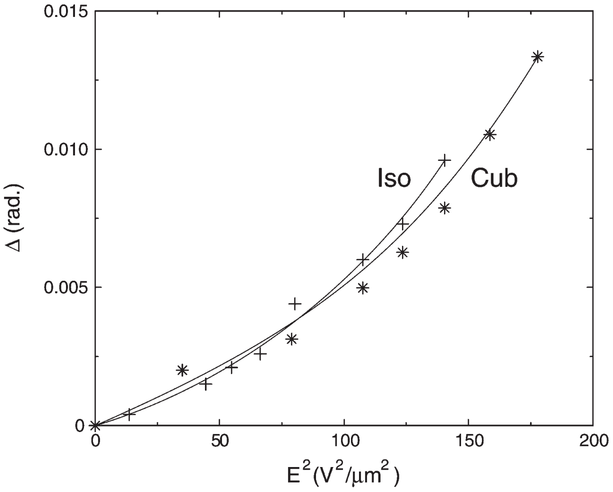

Figure 3. Electric field-induced phase variations of BABH8 in the cell with $d=12.6\,\mu\mathrm{m}$: isotropic phase at 175°C (+), Cub phase at 150°C (*).

response with other Cub LC compounds, we prepared cells by replacing the LC compound with 4'-n-hexadecyloxy-3'-nitrobiphenyl-4-carboxylic acid (ANBC16), which has the phase sequence of crystal 128°C SmC 177°C Cub 199°C SmA 200°C isotropic phases (*10*). In the ANBC16 Cub phase, no AC electric-field response (up to $E{\sim}7\,\mathrm{V\,\mu m^{-1}}$) was found in POM observations.

4. Discussion

The above results show that, for both the BABH8 and ANBC16 Cub phases, the Kerr constants would be as small as those in the isotropic phases. This is remarkably different from the BPs in which the Kerr constant could be 170 times larger than that of nitrobenzene, which is known as a large Kerr constant (isotropic) material (*2*). From the viewpoint of symmetry, BPs (BPI and BPII) and the Cub phase share the same cubic symmetry and an analogy between these phases has been previously pointed out (*11*). In particular, the space group of BPI ($I4_132$) and the Cub phase of BABH8 and ANBC16 (Ia3d) are very close ($I4_132$ and Ia3d are often called single and double gyroids, respectively (*12*)), although the sizes of their 3-D structures are very different. For BP materials, the Kerr constant B can be estimated by (*13*)

$$B \equiv \frac{\delta n}{E^2} = \Delta n \frac{\varepsilon_0 \Delta\varepsilon}{K q^2}, \qquad (1)$$

where δn is the field-induced birefringence and q is the elastic deformation wave number. Δn, $\Delta\varepsilon$ and K are the refractive index anisotropy, dielectric anisotropy and elastic constant of the LC material, respectively. If we apply equation (1) to the Cub phase and compare its Kerr constant to that of a BP material which has similar Δn, $\Delta\varepsilon$ and K, then we can estimate the ratio to be

$$\frac{B_{\mathrm{Cub}}}{B_{\mathrm{BP}}} \sim \frac{q_{\mathrm{Cub}}^{-2}}{q_{\mathrm{BP}}^{-2}} \sim \left(\frac{a_{\mathrm{Cub}}}{a_{\mathrm{BP}}}\right)^2, \qquad (2)$$

where a is the unit cell length of the BP and Cub phase structure. Since typically $a_{\mathrm{BP}}{\sim}200\,\mathrm{nm}$ and $a_{\mathrm{Cub}}{\sim}10\,\mathrm{nm}$, $B_{\mathrm{Cub}}/B_{\mathrm{BP}}$ is of the order of 10^{-3}. Using a typical $B_{\mathrm{BP}}{\sim}10^{-16}\,\mathrm{m^2\,V^{-2}}$, B_{Cub} is therefore of the order of $10^{-19}\,\mathrm{m^2\,V^{-2}}$ (which is about 20 times smaller than that of nitrobenzen (*14*)) and will generate a maximum retardation $d\delta n{\sim}0.06\,\mathrm{nm}$ with $d{=}12\,\mathrm{\mu m}$ under $E{=}7\,\mathrm{V\,\mu m^{-1}}$ (the maximum E tried in Figure 1). The estimated value of the maximum field-induced retardation is negligibly smaller than the value to obtain maximum transmittance in the Kerr cell (~270 nm), and it results in almost no transmittance.

The above estimation result may provide one explanation of why the Cub phase is inactive to electric fields. However, in equation (1), Δn, $\Delta\varepsilon$ and K are macroscopic constants as observed on a smaller scale compared to q_{BP}^{-1}, where nematic order is still present. This assumption on the macroscopic constants may not be fulfilled in the case of the Cub phase as its q_{Cub}^{-1} is of the order of 10 nm. The effective macroscopic values of Δn and $\Delta\varepsilon$ could be very small values in the Cub phase. In any case, the small size (~10 nm) of the Cub phase structure would be the origin of its electric-field inactivity. This is also supported by similar electric-field inactivity (in ITO sandwich cells) that was found in smectic Q phases that have a similarly sized 3-D structure (*15*). This result also gives the insight that, even in the BP case, the shorter the pitch (structural scale) is adjusted so as to minimise the visible wavelength range diffraction and scattering, the higher the driving voltage and the closer to the voltage in the Cub case.

In summary, we have found that the Kerr constants of the Cub phase of BABH8 and ANBC16 are as small as that of the isotropic phases and could be smaller (in contrast to the BP case) than that of some isotropic liquids, e.g. nitrobenzen. This behaviour could be explained by the small structural unit of the Cub phase in comparison to that of the BP.

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