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OBSERVATION OF AMPLITUDE MODE UNDER DC ELECTRIC FIELD IN SMECTIC-Cα* PHASE

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ABSTRACT

OBSERVATION OF AMPLITUDE MODE UNDER DC ELECTRIC FIELD IN SMECTIC-Cα* PHASE. Linear and nonlinear dielectric spectroscopy under DC electric fields has been performed in the high temperature region of smectic-Cα* phase of an antiferroelectric liquid crystal 4-(1-methyl-heptyloxycarbonyl)phenyl 4-octylcarbonyloxybiphenyl-4-carboxylate (MHPOCBC) to obtain a deeper insight of dynamic properties. It is observed a softening of amplitude mode and ferroelectric mode with increasing the DC field close to the smectic-Cα*-smectic-A(C) phase boundary line. It was seen that the relaxation frequency of the amplitude mode obeys the Curie-Weiss law with respect to the applied electric field.

Key words : Dielectric relaxation, Nonlinear dielectric, MHPOCBC, DC field

ABSTRAK

OBSERVASI *AMPLITUDE MODE* PADA MEDAN LISTRIK *DC* DALAM FASA *SMECTIC-Cα.** Telah dilaksanakan pengukuran spektroskopi linier dan nonlinier dielektrik pada medan listrik *DC* dalam daerah suhu tinggi dari fasa *smectic-Cα** kristal cair antiferoelektrik *4-(1-methyl-heptyloxycarbonyl)phenyl 4-octylcarbonyloxybiphenyl-4-carboxylate (MHPOCBC)* untuk memperoleh pemahaman yang lebih dalam tentang sifat dinamik. *Softening* dari *amplitude mode* dan *ferroelectric mode* diamati seiring dengan peningkatan medan listrik *DC* di dekat garis batas fasa *smectic-Cα*-smectic-A(C)*. Perubahan frekuensi relaksasi dari *amplitude mode* terhadap medan listrik yang ditambahkan mematuhi hukum *Curie-Weiss*.

Kata kunci : Relaksasi dielektrik, Dielektrik nonlinier, *MHPOCBC*, Medan *DC*

INTRODUCTION

A precise electric field (E) - temperature (T) phase diagram of 4-(1-methylheptyloxycarbonyl) phenyl 4-octylcarbonyloxybiphenyl-4-carboxylate (MHPOCBC) has been obtained by optical measurements using a photoelastic modulator (PEM) [1,2]. A tricritical point was found on the SmA(C)-SmCα* phase transition line by Bourny et al [3]. A unique field-induced SmCα*-SmC_X* phase and two critical points related to it were found in the low temperature region of the SmCα* phase.

Numerical calculations were made based on a discrete phenomenological model. The results reproduced the experimental ones and it was clarified that the phase has a three-layer structure without spatial modulation. Since the static structures of smectic phases in MHPOCBC have been clarified in the E-T plane, it is interesting to explore the dynamic properties.

The linear and nonlinear electrooptic [4] and dielectric measurements [5,6] have been performed in MHPOCBC without DC electric field. The third-order nonlinear dielectric measurements have given comprehensive results [6]. A Landau-type theory was developed to analyze the frequency dispersions. By utilizing the theory the relaxation frequency of the soft mode in the SmA and the amplitude mode in the SmCα* phase were successfully obtained. The soft mode in this case is a helically tilting mode with a short pitch, generating the structure of SmCα* phase. The relaxation frequency obeys the Curie-Weiss law in both the phases and therefore this is the direct evidence that the SmA-SmCα* phase transition is brought about by the soft mode condensation.

These results demonstrated that the nonlinear dielectric spectroscopy has an outstanding merit that the frequency dispersion of nonpolar soft modes can be measured by means of it, not only in the tilted phases but also in the SmA phase.

Recently, in order to study the dynamic properties in the low temperature region of SmCα* phase, especially through the field-induced SmCα*-SmC_X*-SmC phase transition, the nonlinear dielectric measurements under DC fields around the SmCα*-SmC_X* phase transition have been performed. The softening of a new relaxation mode was observed in SmCα* phase with increasing the DC field close to SmC_X* phase [7]. It might be the soft mode inducing the SmC_X* phase. Meanwhile, there is no report about DC field effect in the high temperature region of SmCα* phase using the nonlinear dielectric spectroscopy.

In this paper, first, E-T phase diagram of MHPOCBC observed by means of the linear dielectric measurements under DC field will be shown. Then, the results of third-order nonlinear dielectric measurements will be reported in order to explore the behavior of amplitude mode under DC field in the high temperature region of the SmCα* phase close to the transition point to the SmA phase.

EXPERIMENTAL METHOD

The sample used in the present experiment was MHPOCBC. The phase sequence of MHPOCBC without electric field is SmA (105.5 ºC) SmCα* (99.5 ºC) SmC_A*. The investigations presented here were all performed in commercially available cells (EHC) with a cell gap of 25 µm. The area of electrodes was (4 x 4) mm^2, and a unidirectionally rubbed polyimide coating for planar alignment. The sample was introduced into a cell in the isotropic phase and it was cooled down slowly to the SmA phase. The sample cell was mounted on a hot stage (Instec HS1).

The complex linear dielectric constants were measured by an impedance analyzer (Hewlett Packard, HP4194A) in the frequency range between 100 Hz and 10 MHz. The driving AC electric field was kept as low as 4 mV/µm to avoid nonlinear effects on the dielectric constant, and a DC biased voltage up to 35 V was applied while performing the DC bias effect measurements to obtain the E-T phase diagram of MHPOCBC. After stabilizing the temperature, the real and imaginary parts of the dielectric constant, ε' and ε'' were measured. In order to avoid the free-charge accumulation due to the application of the biased field, the opposite biased field was applied for the same period of time after each measurement. The measurements were repeated with increasing temperature by 0.1ºC.

Regarding the nonlinear experiments, there is no devices commercially available for measurements of the nonlinear dielectric constants at various frequencies. In general, the nonlinear response is much smaller than the linear one so a precise measurement of nonlinear response is difficult to be done. The measurement system of nonlinear dielectric constant was described in detailed in our previous work [6]. This system utilizes a vector signal analyzer (HP89410A) which allows one to obtain the amplitudes and the phases of the linear and the third-order dielectric responses simultaneously. The frequency dispersions of the sample were measured from 100 Hz to 1 MHz at stabilized temperatures on cooling process with a step of 0.5 ºC. Since the limitation of the equipment, DC field was applied up to 0.64 V/µm.

RESULTS AND DISCUSSION

E-T Phase Diagram of MHPOCBC

Figure 1 shows the E-T phase diagram obtained by plotting the temperature and DC bias field dependences of the real part of the linear dielectric constant, $\varepsilon_1'(\omega)$, measured at 1 kHz on cooling process as a contour plot. The transition temperature between the SmA and SmCα* phases, T_c, is identified from the peak of the linear dielectric constant [6]. The similar E-T phase diagram was also obtained from simultaneous birefringence and tilt angle measurements [1]. The phase boundaries between SmA (SmC) and SmCα*, and SmCα* and SmC_A* are clearly seen. Note contour lines become dense at the boundaries. In the SmA (SmC) to SmCα* transition there exists a tricritical point (designated as A), where the second order phase transition line changes to the first order one. This tricritical point has already been found and investigated in detail by Bourny *et al* [3].

There is a phase boundary between SmCα* and SmC_X* (designated as B) in the low temperature region of SmCα* phase which has been reported by Hiraoka *et al* [8]. Orihara *et al* mentioned that from a theoretical consideration the anomaly is due to a field-induced phase transition and showed from an optical measurement that there is two tricritical points at the end of the line [1]. Another anomaly (designated as C) is observed in the line of SmCα*-SmC phase transition.

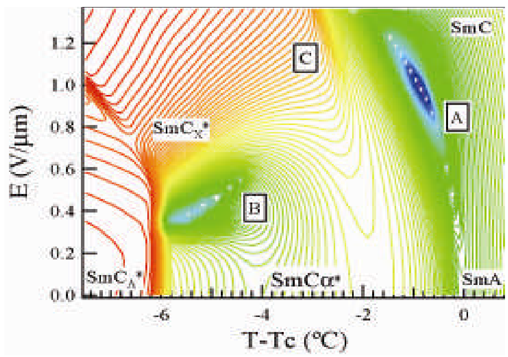

Figure 1. The E-T phase diagram of MHPOCBC obtained from the linear dielectric measurements.The abscissa is a temperature difference from the SmA-SmCα* phase transition temperature, T_c

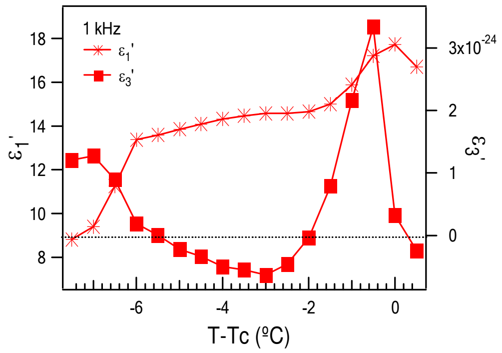

***Figure 2**. Temperature dependences of the real parts of and measured simultaneously on cooling process of 0.5ºC/min at the frequency of 1 kHz and zero dc-field.*

But it cannot be obtained in a cell gap of 13 μm [7]. This might be strongly affected by the surface condition.

Nonlinear Dielectric Response Under DC Field

In order to observe the dynamic properties, the frequency dispersions of the linear and the third-order dielectric constants under DC fields were measured. Figure 2 shows the temperature dependences of the real part of the linear and the third-order dielectric constants measured at 1 kHz and zero DC-field in cooling process.

As shown in Figure 2, the third-order nonlinear dielectric constant shows a complicated temperature dependence behavior in SmA and SmCα* phases. In the SmA phase which is far from the transition point the real part is negative and it increases with decreasing temperature and then it becomes zero above the transition point and the sign changes to positive. In the vicinity of the transition point it increases very steeply and makes a sharp peak below the transition temperature in the SmCα* phase. Orihara et al [5] have successfully explained the anomalous behavior in this phase by using a theory that takes into account the pretransitional fluctuation. In the SmCα* phase, the third-order dielectric constant decreases with decreasing the temperature, as well as the linear one. At about 2ºC below the transition point the value becomes zero and the sign changes to negative. With decreasing temperature, the third-order nonlinear dielectric constant changes from negative to positive, close to the transition point to SmC_A* phase.

Next, we show typical frequency dispersions in the high temperature region of the SmCα* phase close to the SmA phase in Figure 3. It is seen from Figure 3(a) that only the ferroelectric mode, i.e. a homogeneously tilting mode, is involved in the linear dielectric response in the measured frequency region. The increase of dielectric constant at low frequency should be due to ionic conduction. In analysis, therefore, we use the Cole-Cole equation as

$$\varepsilon_1(\omega)=\varepsilon_\infty+\frac{\Delta\chi_f}{1+\left(i\omega\tau_f\right)^{\beta_f}}+\frac{1}{\left(i\omega\tau_i\right)^{\delta}} \qquad ...... \quad (1)$$

where the last term has been added to take the conductivity into account, and

τ_f = Relaxation time of the ferroelectric mode
ε_∞ = Dielectric constant at the high frequency limit
$\Delta\chi_f$ = Dielectric strength
β_f, δ = Distribution parameters

The fitting result using the least square method is shown by solid lines in Figure 3(a). A good agreement was obtained. The distribution parameter β_f was almost 1.

On the other hand, the third-order dielectric response is shown in Figure 3(b), and the frequency dispersion is quite different from that of the first one. In our previous paper [6], the expression for $\varepsilon_3(\omega)$ under zero DC field in the SmCα* has been derived for fitting the frequency dispersion as

$$\varepsilon_3(\omega)=\frac{1}{1+(i2\omega\tau_s)^{\beta_s}}\cdot\left(A_{s1}-\frac{A_{s2}}{(1+i\omega\tau_f)^2}\right)\left(A_{s1}-\frac{A_{s2}}{(1+i\omega\tau_f)(1+i3\omega\tau_f)}\right)+\frac{A_f}{(1+i3\omega\tau_f)(1+i\omega\tau_f)^3} \qquad .... \quad (2)$$

where τ_s and τ_f is the relaxation time of the amplitude mode and ferroelectric mode, respectively. A distribution parameter β_s has been introduced. The solid lines in Figure 3(b) is a theoretical curve, and a good agreement is obtained between the experiment and the theory, where we fixed to be the same value determined from the linear dielectric frequency dispersion, .

Figure 4 shows the frequency dispersions of at different DC electric fields at $T-T_c$ = - 0.5ºC. Due to the limitation of applying DC field to the sample in laboratory-

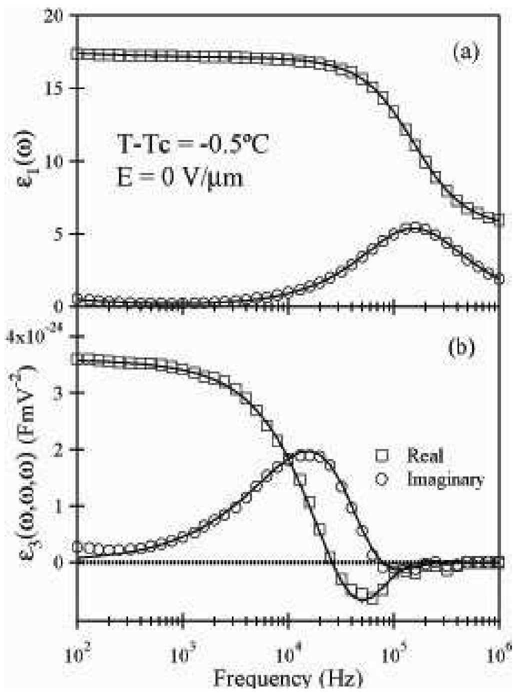

***Figure 3**. Typical frequency dispersions of (a) $\varepsilon_1(\omega)$ and (b) $\varepsilon_3(\omega)$ obtained at $T-T_c$ = -0.5ºC in the SmCα* phase at zero DC field*

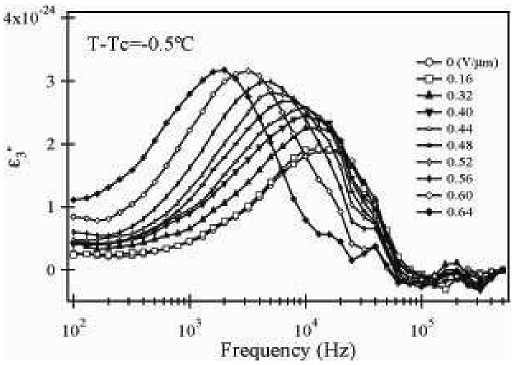

Figure 4. Dependence of the imaginary part of frequency dispersion on dc field in $\varepsilon_3''(\omega)$ at T-T_c = -0.5ºC

made measurement system, the observation were not able to be performed up to the field-induced SmC phase. From Figure 4 it is clearly seen that the peak of the relaxation mode shifts to lower frequencies and the relaxation strength becomes larger with increasing the DC field close to the phase boundary line of the SmA (SmC) phase (see Figure 1). Close to the phase transition temperature the shift is remarkable.

We need an expression for under DC fields to determine the relaxation frequency of the ferroelectric and amplitude modes, but this is quite complicated. Therefore, we used the expression without electric field, which may be a good approximation for small electric fields. The fitting results are shown in Figure 5 for the frequency dispersion data at E = 0.60 V/μm.

Figure 6 shows the DC field dependencies of the relaxation frequencies of the ferroelectric mode and the amplitude mode and obtained from the fitting. The

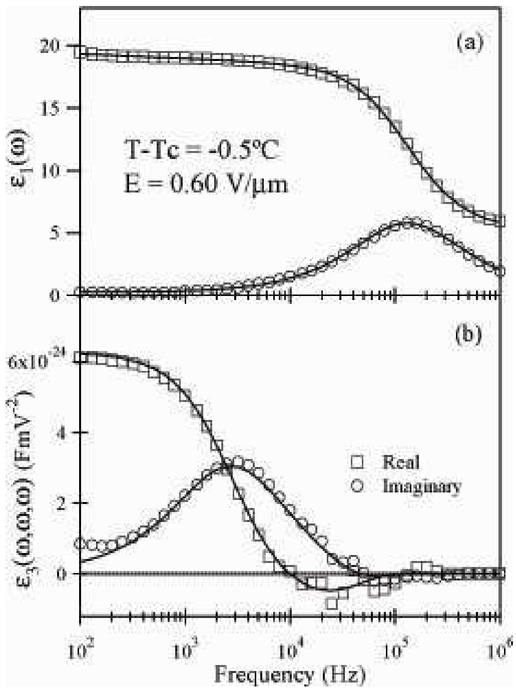

Figure 5. Typical frequency dispersions of (a) $\varepsilon_1(\omega)$ and (b) $\varepsilon_3(\omega)$ obtained at T-T_c = -0.5ºC in the SmCα* phase at E = 0.60 V/μm

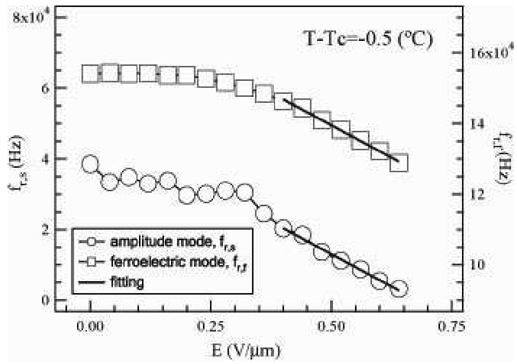

Figure 6. DC field dependences of the relaxation frequencies obtained from the linear and the third-order nonlinear dielectric spectroscopies. and are the relax-ation frequencies of the ferroelectric mode obtained from the fitting result using Eq. (1) and the amplitude mode, respectively

relaxation frequency of the amplitude mode, decreases as increasing the DC field close to the phase boundaries between SmA (SmC) and SmCα*, namely the softening of the amplitude mode takes place. In the high DC field region, the Curie-Weiss law with respect to the applied DC electric field holds for this mode. For the ferroelectric mode, on the other hand, only a partial softening is seen. Note that under electric fields the amplitude and ferroelectric modes are coupled through nonlinear interactions, and so strictly speaking the two modes in Figure 6 appears as a result of the linear combination of these modes. From Figure 6 it is estimated that the soft mode condensation takes place around 0.68 V/μm, which is in good agreement with the value obtained in the E-T phase diagram (see Figure 1).

CONCLUSIONS

The linear and third-order nonlinear dielectric spectroscopy under DC electric fields has been performed in the high temperature region of the SmCα* phase. A softening of the amplitude mode was observed with increasing the DC field close to the SmCα*-SmA(C) phase boundary line by the third-order nonlinear dielectric measurement, as well as a partial softning of the ferroelectric mode by the linear one. It was seen that the relaxation frequency of the amplitude mode obeys the Curie-Weiss law with respect to the applied electric field. Theoretical consideration based on the Landau-type free energy and the detailed measurements of the third-order nonlinear dielectric constants under DC field up to the phase boundary line of SmA(C)- SmCα* are needed to investigate in more detail the dynamic behaviors in the field-induced phase transition.

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