OPTO-ELECTRONICS REVIEW **12**(3), 277–280 (2004)

Non-linear electrooptical effects in chiral liquid crystals

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We studied the electrooptical effects in ferroelectric liquid crystals at both the fundamental and the second harmonic frequency. The linear effects caused mainly by the changes in optic axis position give rise to the changes in the intensity of light passing the sample placed between crossed polarizers. The electric field causes also changes in the shape of the indicatrix. Both mentioned effects influence the second harmonic response. We observed that the defects present in ferroelectric liquid crystal sample affect the electrooptical response to a large extent. This influence is especially significant for the second order harmonics. The depth of light modulation depends on kind of alignment (bookshelf or chevron).

Keywords: liquid crystals, smectics, ferroelectricity, defects, alignment, electrooptical effects.

1. Introduction

Investigations of electrooptical effects in liquid crystals provide a useful information concerning applicability of a given material in various electrooptic devices. The demands for liquid crystalline materials used in photonics or in devices for information visualization are very high. One of the primary parameters is the long-term stability of technical parameters, often connected with the alignment stability of the liquid-crystalline layer. Therefore, the uniform alignment of the liquid crystal sample, without defects or regions with random orientation is of great importance in the device's technology. Electrooptic (EO) measurements are useful in the basic research as well and may deliver information inaccessible with other methods. This statement concerns first of all the investigations of non-linear effects. The measurements of higher harmonics with electrooptic methods are easier than using dielectric methods. Results obtained with electrooptic methods may be used for determination of some material constants connected with either first or second order effects.

The kind and quality of the sample alignment is of great importance for both the kind and magnitude of the electrooptic effects. The multi-domain texture, appearing often as the result of the aging effects, changes the measurement conditions. Similar effects are caused by the changes in the kind of alignment, e.g., from the "bookshelf" to the "chevron" alignment [1]. The mentioned alignment effect is the subject of this paper.

2. Calculations

When an aligned, optically uniaxial liquid-crystalline sample is placed between crossed polarizer and analyser then the intensity of the light I passing the system perpendicularly to the optic axis is described by the form [2]

$$I = I_0\left(\sin^2 2\alpha \sin^2 \frac{\rho}{2}\right), \tag{1}$$

where I_0 is the intensity of incident light, α is the angle between the optic axis and polarization direction of the polarizer. The angle $\rho = 2\pi\Delta n d/\lambda$ denotes the phase lag between the ordinary and extraordinary rays, Δn is the birefringence, d is the sample thickness, and λ is the wavelength of light.

In chiral liquid crystals, characterized by the presence of spontaneous polarization inside each smectic layer, the external electric field E causes linear change of the optic axis direction [3]

$$\alpha = \alpha_0 + aE, \tag{2}$$

where α_0 denotes the azimuth angle α in the absence of electric field and a is a constant. The electric field changes also the shape of the indicatrix [3] what, in turn, affects the phase lag between the ordinary and extraordinary rays ρ

$$\rho = \rho_0 + cE^2, \tag{3}$$

where ρ_0 is the phase lag without field and c is the constant. The changes of both angles α and ρ affect the intensity of light transmitted through the system polarizer–sample–analyser, see Eq. (1). The relative changes in the light intensity (i.e., the modulation depth) can be expressed as [4,5]

$$\frac{\Delta I}{I_0} = EH_1 + E^2(H_{2a} + H_{2c}). \tag{4}$$

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When the electric field is harmonic $E = E_0\cos\omega t$, then ΔI represents the AC component of the light intensity. The term H_1 describes the light modulation at the fundamental frequency ω

$$H_1 = 2\alpha \sin 4\alpha_0 \sin^2 \frac{\rho_0}{2}. \tag{5}$$

The second harmonic intensity consists of two terms

$$H_{2a} = 8a^2 \cos 4\alpha_0 \sin^2 \frac{\rho_0}{2}, \tag{6}$$

and

$$H_{2c} = c \sin^2 2\alpha_0 \sin \rho_0. \tag{7}$$

The term H_1 responsible for the light modulation at the fundamental frequency (linear effect) and the first term of the second harmonic H_{2a} depend only on the coefficient a describing the changes in the position of the optic axis. The second term of the second harmonic depends on both a and c coefficients. These results are valid for different smectic phases (C^*, C_a^*, A). Performing measurements for suitable values of the azimuth angle α_0 one can separate all the mentioned terms and, consequently, determine the a and c coefficients. The terms describing the AC components of the light modulation at the fundamental and the second harmonic frequency are collected in Table 1.

Table 1. Light modulation depth at the first and second harmonic frequency for various azimuth angles.

Equation		$\alpha_0 = 0$	$\alpha_0 = 22.5°$	$\alpha_0 = 45°$
H_1	$2a\sin4\alpha_0\sin^2\rho_0/2$	0	$2a$	0
H_{2a}	$8a^2\cos4\alpha_0\sin^2\rho_0/2$	$8a^2$	0	$-8a^2$
H_{2c}	$2c\sin^2 2\alpha_0\sin\rho_0$	0	c	$2c$

3. Experimental

The measurements have been performed for the ferroelectric mixture FELIX 015-100 from Hoechst. This material has a broad range of the ferroelectric smectic C^* phase (from below the room temperature up to 72°C). For this reason it has large application potential. The electrooptic experiments have been performed using commercially available 5-µm thick cells from Linkam (UK). These cells consist of glass plates equipped with semitransparent electrodes and rubbed polymer orienting layers. The liquid-crystalline mixture was introduced into the cell in its isotropic phase (above 86°C) by capillary action. Homogeneous planar alignment was achieved by slow cooling from the isotropic phase to the smectic A phase (72–82°C). The alignment was furthermore improved by applying low frequency electric field (about 10 Hz) of high amplitude (about 10 V/5 µm) in the smectic C^* phase. This procedure resulted in a well-aligned sample in "bookshelf" geometry, i.e., with smectic layers perpendicular to both the substrates and the rubbing direction. The sample was placed in a modified Mettler hot stage. The temperature of the stage

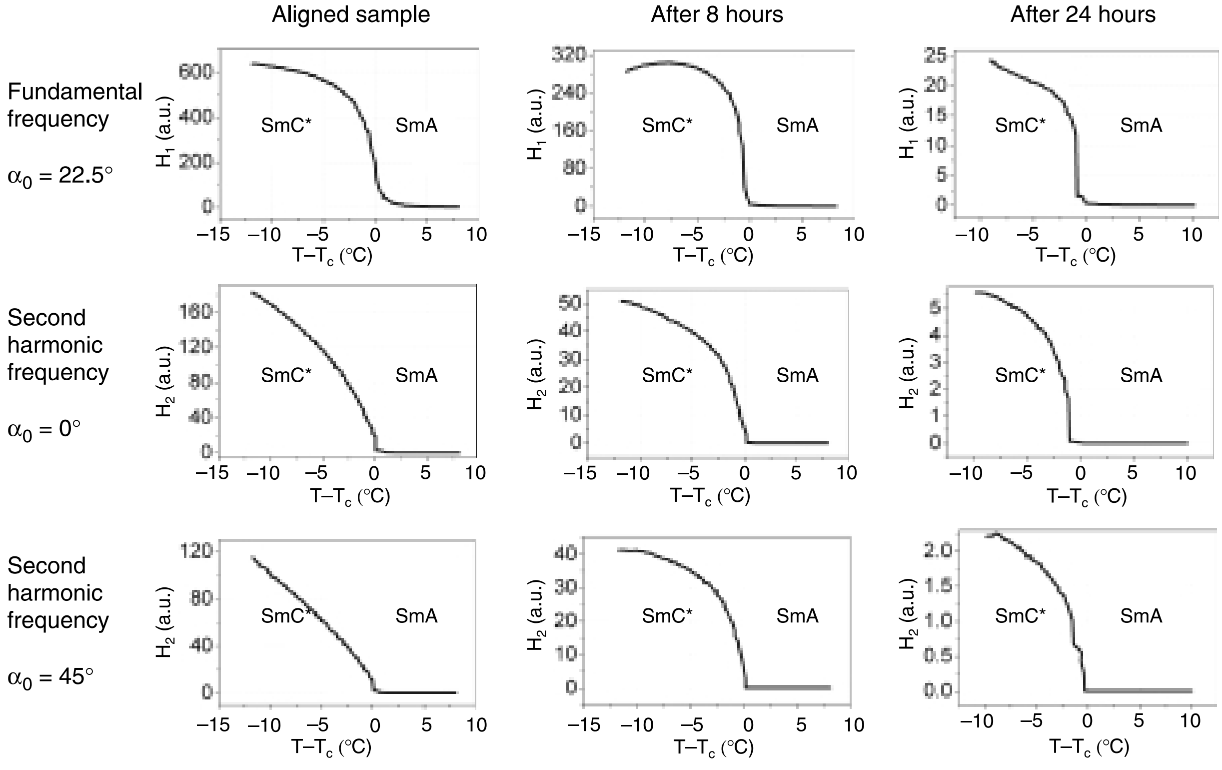

Fig. 1. The time changes of temperature dependencies of the modulation depth for the first and second harmonics.

was controlled by the Digi-Sense controller of TC 9500 type. The sample was placed under the polarizing microscope Axioskop from Zeiss (Germany). An AC voltage from the oscillator DS 340 (Stanford Research, USA) was applied to the electrodes. The changes in the light intensity were registered using the photodiode with the preamplifier PIN20 (FLC Electronics, Gothenburg, Sweden). The output of the preamplifier was connected to the input of the lock-in amplifier SR 530 (Stanford Research). Both the measuring process and the data acquisition were controlled by a personal computer.

4. Results and discussion

The electrooptical effects have been measured as function of temperature and azimuth angle by applying AC voltage of 0.5 V amplitude and frequency 440 Hz. The angle between the polarization direction and the optic axis was 22.5 deg in the case of the first harmonic. To avoid influence of the linear effect, the modulation at doubled frequency was measured for $\alpha_0 = 0$ and $\alpha_0 = 45$ deg. During the measurements we noticed that the results obtained in successive runs considerably differed – the electrooptic response decreased with time. The simultaneously performed texture observations revealed increasing number of defects present in the sample. To check the influence of defect number on the electrooptic response we prepared a fresh, well-aligned sample and performed the measurement of the modulation depth for both first and second harmonics as a function of time. The results are shown in Fig. 1.

The first measurement has been done immediately after preparing the sample, and the next measurements after 8 and 24 hours, respectively. The second harmonics was measured for two azimuthal angles indicated in the figure. As the figure demonstrates, intensity of the electrooptical response diminishes considerably with time, although the shape of the temperature dependencies remains almost unchanged. Figure 2 presents the time dependence of the first harmonic measured at a room temperature (25°C). Typical textures registered simultaneously are also shown. It is obvious that the modulation depth decreases as the number of defects increases.

The measuring electric field (0.5 Vrms, 440 Hz) was applied only during measurement for about 1 minute. The AC component of the light intensity decreases initially very quickly, eventually slower and slower. About 1 day after preparation, the optical response stabilizes at low level amounting to a few percent of the starting value. At the moment indicated by the letter A in Fig. 2, electric field 10 V, 10 Hz was applied to the sample for a few minutes resulting in evident improvement in the alignment quality, now comparable with the initial alignment (compare photos 1 and 4 in Fig. 2). After improving the alignment quality, the modulation depth has came back to its initial value. Thus, the applied alignment procedure works well and can be used to secure the reproducibility of electrooptic measurements. It was exploited in all experiments described below, aimed at verification of the calculation results presented in the former section.

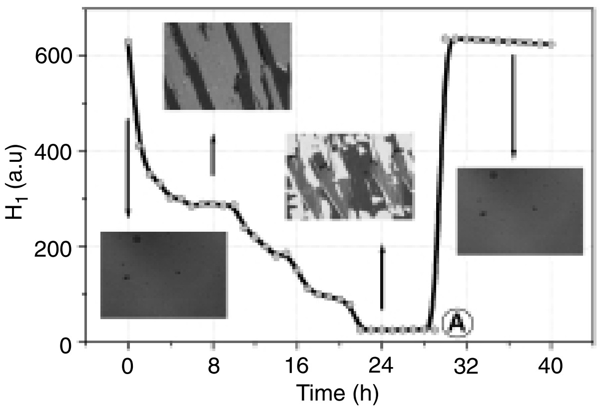

Fig. 2. Electrooptical response at the fundamental frequency as function of time and typical textures (magnification 240×) observed during the measurement. The letter A shows the instant when the sample was refreshed using low frequency electric field (see text for details).

To prove Eqs. (5), (6), and (7) describing the light modulation at the fundamental and second harmonics, AC voltage was applied to the electrodes and the AC component of the light intensity was registered, as described before. To enhance the second harmonics signal, the applied voltage has relatively large value of 1 V rms. Figure 3 demonstrates the results of experiments. In every oscilloscope picture the upper curve represents the applied voltage and the lower curve – the electrooptical response. The measurements were carried out in various phases (ferroelectric smectic C*, paraelectric smectic A and cholesteric N*). In the smectic C* phase, the signal of double frequency is present for arbitrary values of the azimuthal angle α_0. The signal of fundamental frequency is absent for $\alpha_0 = 0$ and $\alpha_0 = 45$ deg having its maximum for $\alpha_0 = 22.5$ deg. All mentioned observations are in agreement with Eqs. (5), (6) and (7). In the smectic A phase, the response at basic frequency is maximum for $\alpha_0 = 22.5$ deg and the response at double frequency is practically absent. This observation can be used for unambiguous identification of the phase transition to the Sm A phase. In the cholesteric phase, as expected, the electrooptic modulation is very weak. As Fig. 3 demonstrates, the first and second harmonics of the electrooptic modulation can be separated by suitable choosing of the initial azimuthal angle α_0.

In practice, both linear and quadratic electrooptic effects appeared simultaneously. The experiment has confirmed theoretical predictions (Eqs. 5, 6, 7) concerning the characteristic behaviour of the linear and quadratic response. Equations (5), (6), and (7) describe also the dependence of the electrooptic modulation on the azimuth angle α_0. Figure 4 demonstrates the agreement of these equations with experiment.

If the correct alignment of the sample is preserved during the whole experiment (what can be done using the pro-

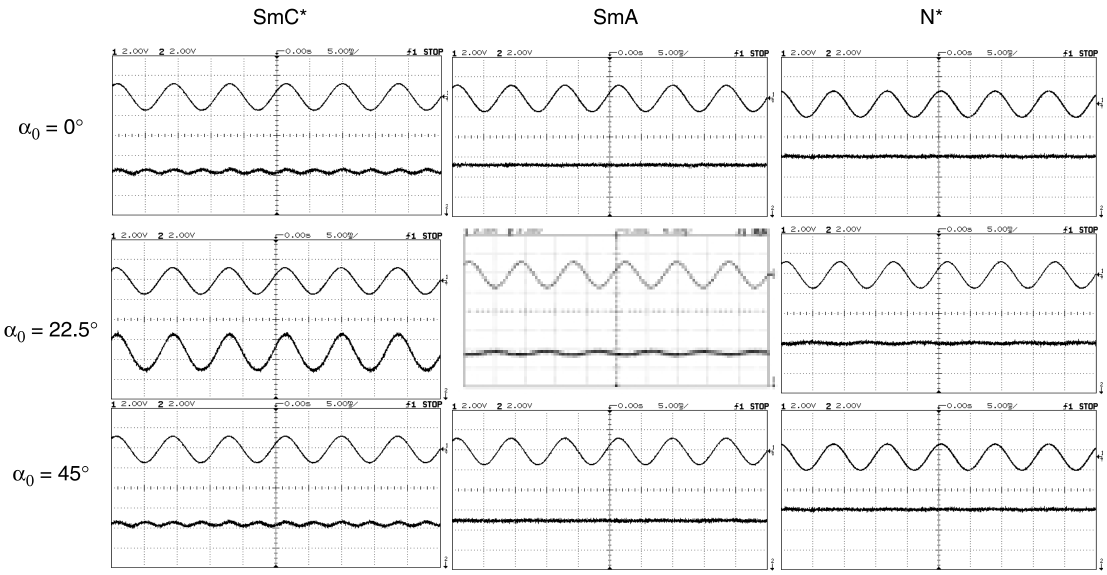

Fig. 3. Oscilloscope pictures of the electrooptical response (lower curves) in different phases and for different azimuthal angles α_0.

cedure described earlier), the coefficients *a* and *c* can be determined from the angular dependence of the second harmonic intensity. The knowledge of these parameters allows for the determination of various material parameters of the sample, like elasticity and viscosity coefficients and dielectric anisotropy of the smectic layer.

5. Conclusions

The simplest way to determine material parameters of the smectic C* phase is to use the so-called "bookshelf" geometry. To obtain this kind of alignment polymer orienting layers and electric or magnetic fields are often used. After switching the electric field off, the molecules tend to an orientation with the lowest value of free energy. In materials with non-zero spontaneous polarization, this causes a kind of compensation of polarization. Domains with different direction of the polarization vector appear and the alignment becomes non-homogeneous. Then, often the so-called "chevron" [1] geometry occurs. The simplest way to avoid this effect is to apply the external AC voltage permanently or performing the described alignment procedure before the experiment.

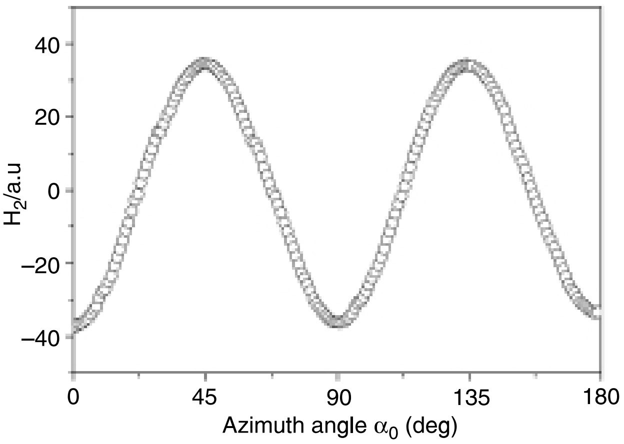

Fig. 4. Dependence of the second harmonic modulation intensity on the azimuthal angle α_0.

The results of performed experiments are in agreement with the results of calculations of the first and second harmonics intensity. The experiments demonstrated that separation of the harmonics could be performed easily by suitable choice of the initial azimuthal angle. Determination of the coefficients *a* and *c*, describing the electric field effect on the optical properties of the sample can be done by measurements of the second harmonics at different azimuthal angles. These parameters deliver valuable information on the structure of tilted smectic liquid crystals and its dependence on the electric field.

Acknowledgments

This work was supported by the State Committee for Scientific Research (KBN) in the framework for the project 2PO3B 127 22.

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