

Optical imaging of ferroelectric domains in periodically poled lithium niobate using ferroelectric liquid crystals

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Abstract

Ferroelectric liquid crystals exhibiting a chiral smectic C* phase are deposited on z-cut periodically poled lithium niobate substrates and investigated by polarized optical microscopy. While the pure substrates placed between crossed polarizers and observed in transmission appear dark, uniformly aligned liquid crystal films deposited on these substrates show alternating domains with varying brightness. This effect can be attributed to the well-known coupling between the direction of the spontaneous polarization and the optical axis in the birefringent ferroelectric smectic C* phase. Quantitative measurements of the tilt angle between the local optical axis and the smectic layer normal confirm antiparallel orientations of spontaneous polarization of the liquid crystal from domain to domain, as expected by the periodic poling of the lithium niobate substrate. This effect provides a valuable non-destructive method of optical inspection of the quality of periodically poled ferroelectric substrates, which plays an important role in achieving quasi-phase-matching in non-linear optical applications.

1. Introduction

Both crystals and liquid crystals (ordered fluids) may show various contributions to the components of the electric polarization:

$$P_i = P_{s,i} + \varepsilon_0 \chi_{ij}^{(1)} E_j + \varepsilon_0 \chi_{ijk}^{(2)} E_j E_k + \varepsilon_0 \chi_{ijkl}^{(3)} E_j E_k E_l + \dots, \quad (1)$$

where E_j , E_k , E_l with $j, k, l \in \{1, 2, 3\}$ are the components of the electric field in the three-dimensional space [1, 2]. The Einstein notation, i.e., summation over repeated indices, is implied in (1). Crystals with polar ordering, such as lithium niobate, may show ferroelectricity, i.e., a spontaneous polarization $\mathbf{P}_s \neq 0$, as well as non-vanishing components of the third-rank tensor $\chi^{(2)}$. The non-linear susceptibility $\chi^{(2)}$ describes phenomena like linear changes of the refractive indices under the influence of a quasi-static

electric field (Pockels effect) or frequency conversion of electromagnetic waves, such as sum and difference frequency generation or second harmonic generation. The efficiency of these non-linear optical effects is impeded by dispersion, which causes phase differences between the exciting pump wave and the generated radiation. To overcome this problem, a quasi-phase-matching scheme is usually applied, which is obtained by a periodical inversion of crystal domains [3]. Such periodically poled lithium niobate (PPLN) crystals or waveguides fabricated in PPLN are used for various types of optical frequency converters.

Thin slabs of lithium niobate crystals, which are cut perpendicular to the polar axis (z-axis) and exhibit an alternating poling of \mathbf{P}_s (z-cut PPLN substrates), have shown to be very efficient in integrated non-linear optical devices. Domain walls in these structures have been studied previously by confocal Raman microscopy [4] or second harmonic (SH) microscopy [5]. In a previous study [6],

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atomic force microscopy (AFM) was modified by applying an AC electric field to the cantilever and measuring the phase shift between the applied AC signal and the resulting periodic cantilever deflection using a lock-in amplifier (Fig. 1). However, this technique of electrostatic force microscopy (EFM) is not a readily available standard method. Unfortunately, the success of the poling procedure cannot be tested simply by polarization optical microscopy, because the z -cut crystals exhibit apparently optical isotropy for light propagating along the z -axis. Apart from SH microscopy, the most common method to visualize the domain is wet etching using HF-acid, which exploits the different etching speeds of $+z$ - and $-z$ -oriented surfaces [7]. However, for integrated optical devices, with waveguides directly at the surface, the method is destructive as it produces a surface relief, which leads to high propagation losses in the waveguide.

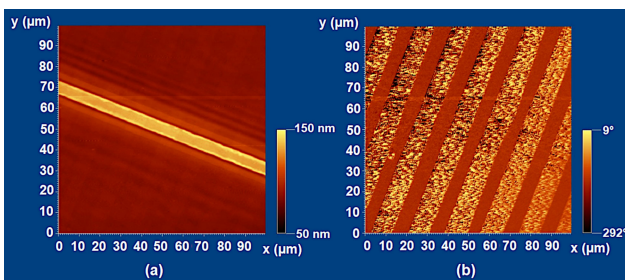


Fig. 1. Optical waveguide on PPLN. (a) Topography is measured by AFM, which shows the waveguide fabricated by titanium deposition. (b) Periodic poling of the same sample, visualized by measuring the phase shift of the periodic deflection of the cantilever when an AC electric field (frequency of 2 kHz) is applied. For details, see Ref. 6.

In this work, we present an alternative method to visualize periodic poling more easily by utilizing a liquid crystal (LC). LCs consist frequently of rod-like or disk-like molecules, which are preferably parallel aligned to each other and show birefringence due to the anisotropy of the susceptibility tensor $\chi^{(1)}$. In addition, some liquid crystalline mesophases show ferroelectricity, i.e., $\mathbf{P}_s \neq 0$, as well. In rare cases, the spontaneous polarization and the resulting ferroelectric properties originate from a parallel alignment of the dipole moments of neighbouring molecules along the optical axis of the LC [8–11]. However, typically, the permanent dipole moments of neighbouring molecules along the optical axis are antiparallel, thereby compensating each other. If so, only a hindered rotation of molecules may give rise to a non-zero-sum of lateral components of their dipole moments. The spontaneous polarization is oriented perpendicular to the optical axis of the LC in this case. This scenario is observed, for example, in tilted columnar phases of chiral disk-like molecules [12], in tilted lamellar (smectic) phases of bent-core molecules [13], and most frequently in tilted smectic phases of chiral rod-like molecules [14–16]. In the present investigation, a chiral tilted smectic C (SmC*) phase is used. In this phase, chiral rod-like molecules are arranged in layers. The preferred direction of the long axes of molecules, which can be described by the director \mathbf{n} , deviates from the layer normal \mathbf{z} by a tilt angle θ (Fig. 2). The pseudo vector \mathbf{n} corresponds to the principal symmetry axis of the susceptibility tensor $\chi^{(1)}$ and indicates the local optical axis of

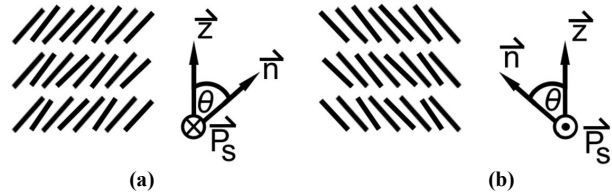


Fig. 2. Structure of the ferroelectric SmC*-phase.

an optically uniaxial birefringent domain. For symmetry reasons, the spontaneous polarization \mathbf{P}_s is perpendicular to the layer normal \mathbf{z} and the director \mathbf{n} , as expressed by the relation:

$$\mathbf{P}_s = P_0(T) \cdot \mathbf{z} \times \mathbf{n}. \quad (2)$$

If a helical structure of the director field $\mathbf{n}(\mathbf{r})$, which may occur in chiral LCs, is suppressed by confinement between aligning planar substrates and if the layer normal \mathbf{z} is uniformly aligned parallel to the substrates, reorientation of the spontaneous polarization \mathbf{P}_s by an external electric field \mathbf{E} perpendicular to the LC layer causes an in-plane reorientation of the optical axis by a switching angle of 2θ (Fig. 2). By means of crossed polarizers, this switching effect is used in surface stabilized ferroelectric liquid crystal (SSFLC) displays [17]. The coupling between the director orientation to the spontaneous polarization of a LC and its interaction with the spontaneous polarization of a ferroelectric crystal was also used in previous studies to investigate the polarization direction at the surface of pristine lithium niobate [18]. Whether this method is useful for a non-destructive assessment of the quality of PPLN substrates is investigated in the present work.

2. Experiments and results

The PPLN substrates used in this study are 0.5 mm thin slabs of lithium niobate crystals, which are cut perpendicular to the polar axis (z -axis) and exhibit an alternating poling of \mathbf{P}_s with a spatial periodicity of $\Lambda = 16.9 \mu\text{m}$. Their interaction with a ferroelectric liquid crystal (FLC) is investigated by polarization optical experiments. To facilitate availability, we have chosen two commercially available FLC mixtures – Felix R&D (Hoechst) [19] and ZLI3654 (Merck) [20]. Since the precise compositions of these mixtures are not known, a self-made mixture consisting of 80 mol-% 5-*n*-octyl-2-(4-*n*-octyloxy-phenyl)-pyrimidine (PYP 808) and 20 mol-% 4-(3-methyl-2-chlorobutanoyloxy)-4'-heptyloxybiphenyl (A7) [21, 22] (Fig. 3) is tested, in addition. The pure compound A7 is known to exhibit a ferroelectric SmC* phase with unusually large spontaneous polarization ($P_s > 100 \text{ nC/cm}^2$) [21].

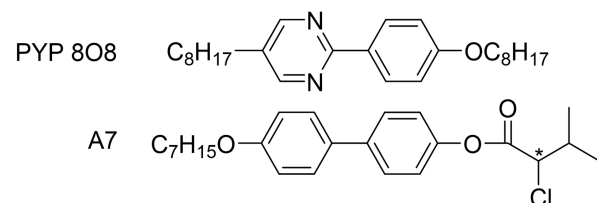


Fig. 3. Chemical structures of the compounds PYP 808 and A7, which compose one of the investigated FLC mixtures.

The composition of the mixture PYP 808 /A7 was chosen to provide the appearance of the SmC* phase at room temperature [22]. All three mixtures are expected to show a ferroelectric SmC* phase at temperatures in the vicinity of room temperature.

2.1. Characterisation of the LCs

The phase transition temperatures of the three FLC mixtures mentioned above were measured by differential scanning calorimetry (DSC) using a Phoenix 204 F1 instrument (Netzsch). All investigated FLC mixtures exhibit the same phase sequence C-SmC*-SmA*-N*-I, with their ferroelectric SmC* phase either at room temperature [Felix R&D (Hoechst) and ZLI 3654 (Merck)] or close to room temperature (80 mol-% PYP 808/20 mol-% A7) (Table 1).

The electro-optic properties were characterised using commercial test cells from EHC Co., Ltd, Tokyo, Japan ($d = 2 \mu\text{m}$, coated with a 180° rubbed polyimide alignment layer on both sides). The temperature dependence of the spontaneous polarization P_s was measured using the triangular wave method ($U = 5\text{V}$, $f = 100\text{Hz}$, Fig. 4) [23].

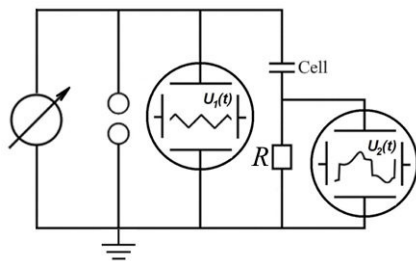


Fig. 4. Circuit used for measuring the spontaneous polarization P_s of the LCs.

An FP82 microscope hot stage and an FP90 controller (Mettler) were used to control the temperature. For measuring the switching times τ , square waves were applied to the same test cells. The respective sample was placed between crossed polarizers and illuminated with white or monochromatic light. The transmitted light intensity vs. time was measured in the range of linear electro-optic response and fitted to a single exponential to achieve the switching time τ at the respective temperature. Multiplying the switching time τ with the spontaneous polarisation P_s and the applied electric field strength E yields the rotational viscosity $\gamma_\phi = \tau \cdot P_s \cdot E$. This electro-optic characterisation reveals values of the spontaneous polarization P_s between 0.67 nC/cm^2 and 5.7 nC/cm^2 , sub-millisecond switching times, and rotational viscosities below 0.1 Pas (Fig. 5). Typical for FLCs, the values of P_s , τ , and γ_ϕ decrease with increasing temperature. The mixture containing the compound A7 shows the largest spontaneous polarization (as expected), but also a larger viscosity. The variety of different values of P_s and γ_ϕ for the three FLC mixtures facilitates discussing the influence of these parameters on the LC alignment at a PPLN surface.

2.2. Test cells made of two glass substrates equipped with only one alignment layer

The fabrication and the electro-optic properties of SSFLC displays are well-known. In SSFLC cells, a thin layer of the FLC is sandwiched between two glass plates, with each of the inner surfaces being coated by an aligning layer. Typically, these aligning layers consist of polyimide and are unidirectionally rubbed to achieve the parallel alignment that is necessary. However, a direct contact of the FLC with a PPLN substrate without any polymer layer

Table 1.

Measured phase transition temperatures of the FLC mixtures investigated.
 C: solid crystal; SmC*: chiral smectic C phase; SmA*: chiral smectic A phase;
 N*: chiral nematic (= cholesteric) phase; I: isotropic liquid phase.

FLC Mixture	Phase Sequence	Ref.
Felix R&D	C 2.1 °C SmC* ~ 51.0 °C SmA* 58.7 °C N* 68.1 °C I	[17]
ZLI 3654	C -38.0 °C SmC* ~ 59 °C SmA* 68.3 °C N* 81.1 °C I	[18]
PYP 808 / A7 (80:20)	C 27.1 °C SmC* ~ 50.8 °C SmA* 62.8 °C N* 65.1 °C I	[19]

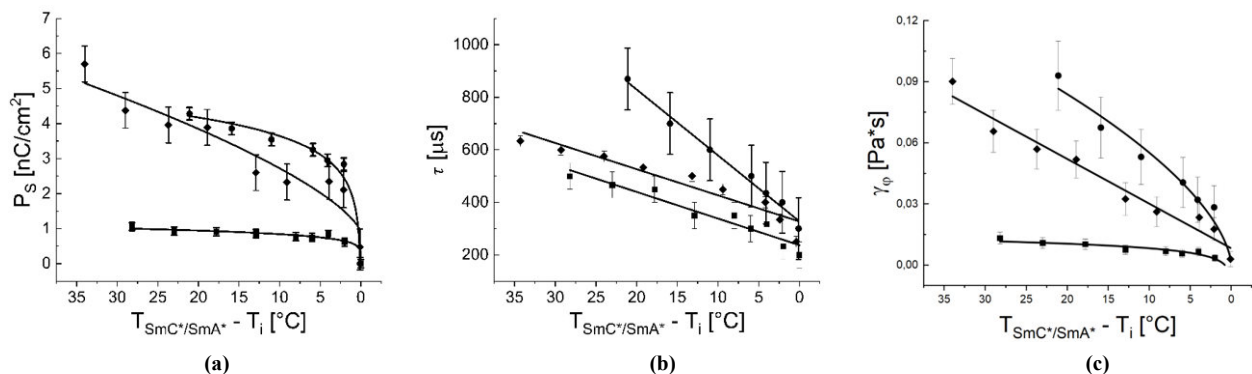


Fig. 5. Experimental values of the LC properties vs. reduced temperature. (a) Spontaneous polarization P_s , (b) switching time τ , (c) rotational viscosity γ_ϕ . (■) Felix R&D, (◆) ZLI 3654, (●) PYP 808/A7 (80:20).

in between was wanted in the present study. To achieve a uniform FLC alignment under this condition was particularly challenging. To test whether the uniform alignment can be achieved using only one aligning layer, preliminary experiments were performed on test cells consisting of two glass plates, one of which (purchased from EHC. Co., Ltd., Japan) was equipped with a commercial alignment layer made of rubbed polyimide [PI, resin LX-1400 (manufactured by Hitachi Chemical Co., Ltd., coating thickness 200 Å or thinner)], while a clean glass plate without any alignment layer was used as a counter substrate (Fig. 6). No spacers were used. According to Ref. 18, the expected sample thickness is $\approx 1 \mu\text{m}$. The respective cell was filled with the FLC at an elevated temperature, where the isotropic phase appeared. Eventually, the resulting cell was annealed by heating and cooling in the vicinity of the phase transition temperature between the SmC* and the SmA* phase. The quality of alignment before and after annealing was observed via polarized optical microscopy (POM). The tilt angle was found by placing the sample on a rotating stage between crossed polarizers and finding the azimuthal angle corresponding to minimum transmission intensity.

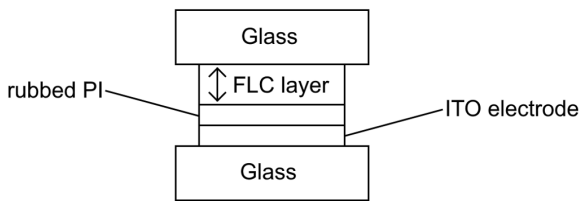


Fig. 6. Test-cell for preliminary studies of the alignment behaviour and for measuring the tilt angle.

The investigated test cells with only one aligning substrate coated with rubbed PI and a clean glass plate without an alignment layer as a counter-substrate show a very poor alignment after being filled with the respective FLC [Fig. 7(a)]. However, annealing of the sample by repeated heating and cooling at temperatures in the vicinity of their respective phase transition temperature SmC*/SmA* leads to a substantial improvement of the FLC orientation. Placing the sample between crossed polarizers on the rotating state of an optical polarizing microscope with the plane of polarization of incident light parallel to the rubbing direction and rotating the sample reveals a spatially uniform brightness of the sample [Fig. 7(b)], the transmitted light intensity depends strongly on the azimuthal angle of the rotating sample. This indicates uniaxial birefringence and

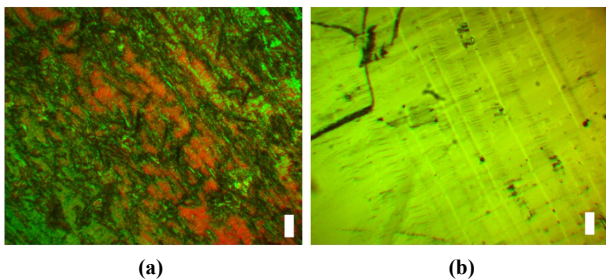


Fig. 7. Improvement of FLC-orientation: Appearance of a test cell with 80 mol-% PYP 808 / 20 mol-% A7 at 28.0 °C in a polarizing microscope with crossed polarizers (a) before and (b) after annealing around $T_{\text{SmC}^*/\text{SmA}^*}$. The vertical scale bars correspond to 100 μm .

uniform in-plane alignment of the optical axis of the FLC. However, the orientation of the optical axis, which can be measured by finding the dark state, deviates systematically from the rubbing direction of the PI alignment layer. This observation agrees with the well-known behaviour [11–13] that the layer normal z (as opposed to the director \mathbf{n}) is aligned along the rubbing direction. Rotating the sample to the dark state and measuring the deviation of the azimuthal angle of this state from the rubbing direction yields the intrinsic tilt angle θ of the tilted smectic phase (Fig. 2). All three FLC mixtures show very similar behaviour to the example shown in Fig. 7. The experimental values of the respective tilt angles are given in the second column of Table 2.

Table 2.

Experimental tilt-angles θ and θ_{PPLN} , measured in test cells made of one aligning glass substrate and a counter substrate made of bare glass (θ) and made of PPLN (θ_{PPLN}), respectively.

FLC Mixture	θ [°]	θ_{PPLN} [°]
Felix R&D	13.5	13.75
ZLI 3654	24.0	23.19
PYP 808 / A7 (80:20)	15.3	15.35

2.3. Investigation on PPLN with one aligning counter-substrate

The PPLN crystal under investigation [Fig. 8(a) and (b)] shows periodically poled ribbons with a width of 7 μm each that are arranged in triples with a lateral distance of 100 μm between neighbouring ribbons [Fig. 8(b)]. Please note that this design differs from the sample shown in Fig. 1. The crystal was first cleaned in acetone, in isopropanol and in distilled water for 10 min in each solvent. The respective FLC mixture was confined between a standard single test substrate (from EHC. Co., Ltd., Japan) with a rubbed polyimide alignment layer (LX-1400) and the PPLN crystal at the clearing temperature [Fig. 8(c) and (d)]. The PI rubbing (y -) direction is perpendicular to the (x -) direction of the ribbons. Again, no spacers were used, i.e., the sample thickness is approximately 1 μm [18]. The resulting cell was annealed around the phase transition temperature SmC*/SmA* and observed via POM. The apparent tilt angle was measured as described above. After the measurements, the cells could easily be disassembled, cleaned with acetone, isopropanol and distilled water, and reused for the next test or for other purposes.

The investigation of samples consisting of a PPLN substrate, and an aligning counter substrate made of glass and a rubbed PI layer show essentially the same behaviour as the test cells described in the previous section. In pristine samples immediately after filling the sample with one of the FLC mixtures, the LC alignment is very poor and seems not to be affected by the PPLN substrate. However, annealing of the respective sample close to the SmC*/SmA* phase transition temperature gradually improves the alignment until most of the area of the sample shows a uniform brightness that depends on the azimuthal orientation of the sample between crossed polarizers. In this uniform state, the periodic poling structure of the PPLN substrate can clearly be seen by means of POM for

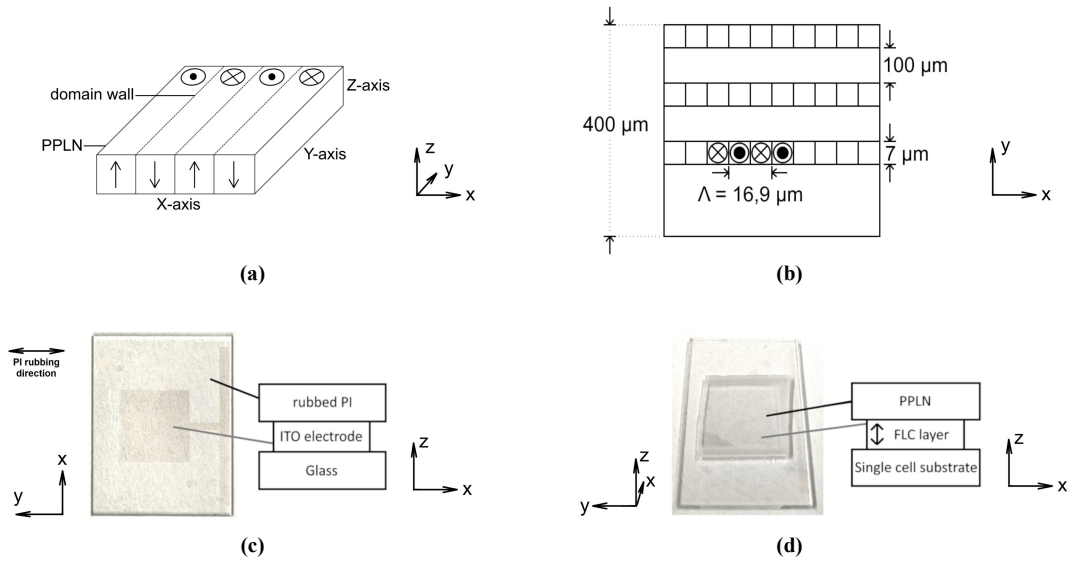


Fig. 8. Investigated structures. (a) Side view of the PPLN crystal. (b) Top view of the PPLN crystal. (c) Glass substrate from EHC. Co., with a transparent ITO electrode in the center (1 cm × 1 cm), coated with rubbed polyimide (PI). (d) LC consisting of a bottom glass plate [as shown in part (c)] and a PPLN substrate on top.

all three FLC mixtures (Fig. 9). Comparison with a micrometer scale reveals a longitudinal domain width of the periodically poled stripes of $(8.4 \pm 0.1) \mu\text{m}$, which matches the expected value of $\frac{\Lambda}{2} \cong 8.45 \mu\text{m}$.

Closer optical inspection of the FLC-PPLN cells in transmission while rotating the cell between crossed polarizers (Fig. 10) shows that there are azimuthal orientations ($\varphi = 0$ in Fig. 10), where the contrast between

neighbouring domains along the periodically poled chain almost vanishes. In the vicinity of this orientation, there are two orientations ($\varphi = +13.5^\circ$ and $\varphi = -14.0^\circ$ in Fig. 10), where every second domain along the periodically poled chain appears dark so that maximum optical contrast between the domains is achieved. Dark appearance of a domain indicates that its optical axis is parallel (or perpendicular) to the plane of polarization of the incident

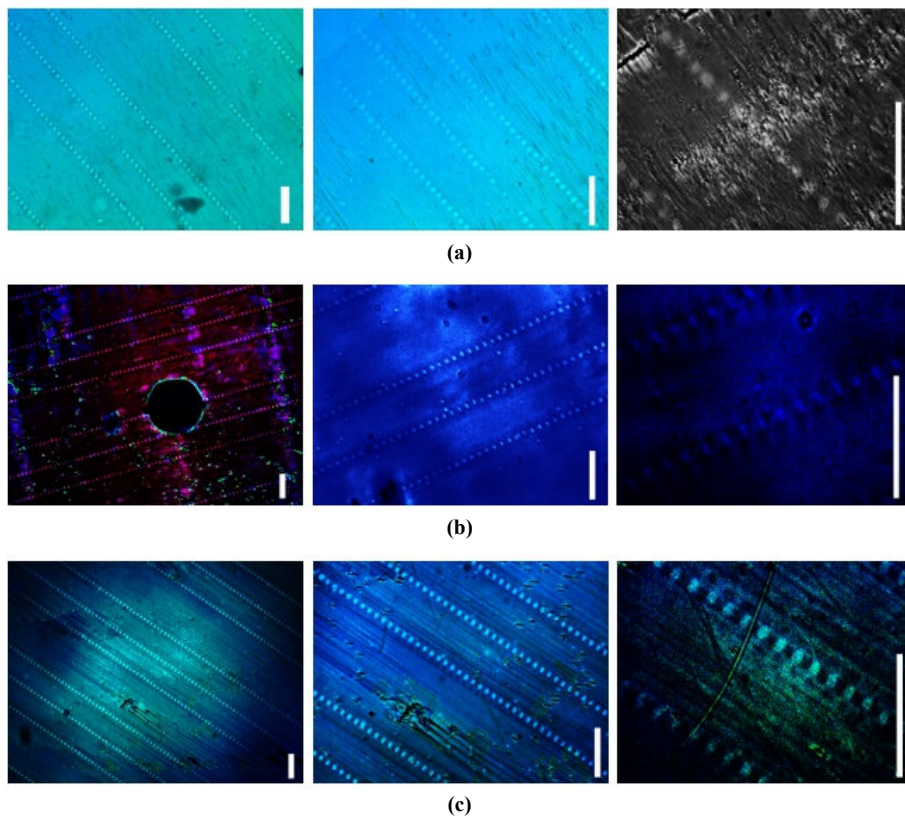


Fig. 9. POM images of the FLC-on-PPLN-cells. The vertical scale bars correspond to 100 μm. (a) Felix R&D (Hoechst) at room temperature, (b) ZLI 3654 (Merck) at room temperature, (c) PYP 808 / 7 (80:20) at 28.0 °C.

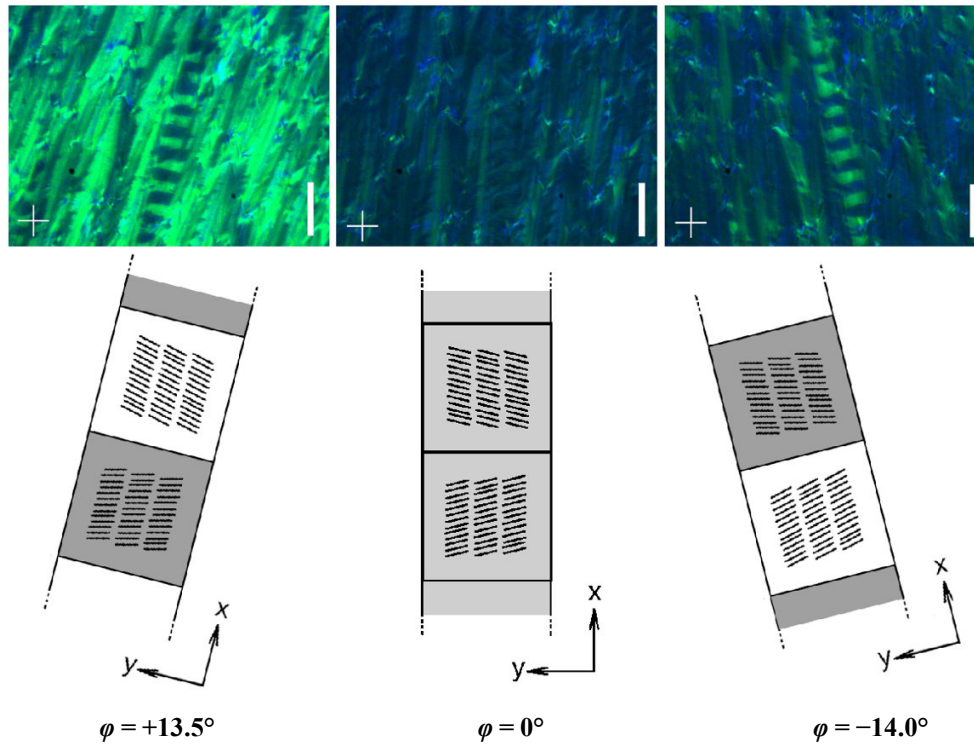


Fig. 10. Appearance of an FLC-PPLN cell with Felix R&D at room temperature between crossed polarizers (plane of polarization vertical and horizontal, respectively) for different azimuthal orientations of this cell.

light. The same domains which appear dark at $\varphi = +13.5^\circ$ appear bright at $\varphi = -14.0^\circ$ and *vice versa*. So, obviously, the projections of the optical axes to the cell plane differ by $\Delta\varphi = +13.5^\circ - (-14.0^\circ) = 27.5^\circ$ from domain to domain.

From the difference $\Delta\varphi$, we calculated apparent tilt angles $\theta_{PPLN} = \frac{1}{2} \cdot \Delta\varphi$, which are given in the third column of Table 2. If the spontaneous polarizations of neighbouring FLC domains are perpendicular to the substrate and antiparallel to each other like the two electro-optic switching states of an SSFLC [14] that are shown in Fig. 2, we expect $\theta_{PPLN} = \theta$, where θ is the intrinsic tilt angle of the respective SmC* phase given in the second column of Table 2. In contrast, we would expect the apparent tilt angle θ_{PPLN} to be smaller than the intrinsic tilt angle θ , when the directions of the spontaneous polarization of the FLC domains deviate from the surface normal. Table 2 shows that the tilt angles θ_{PPLN} and θ are in good agreement within the experimental error of $\pm 1^\circ$ for each of the FLC mixtures. This finding indicates that the spontaneous polarizations of neighbouring FLC domains are perpendicular to the substrate and antiparallel to each other, as expected for the spontaneous polarizations of the respective PPLN substrate. So, the optical appearance of the FLCs confirms the good quality of the PPLN substrates.

3. Conclusions

In summary, three different SmC*-mixtures [FLC Felix R&D (Hoechst), ZLI 3654 (Merck)] and a mixture of 80 mol-% PYP 808 and 20 mol-% A7 were used to image the ferroelectric domains in PPLN. One could speculate whether the success of the FLC alignment on a ferroelectric crystal surface requires a sufficiently large spontaneous

polarization of the FLC or may be limited by the viscosity. However, all three mixtures turned out to be useful for this purpose and confirmed good quality of the periodically poled domains in the lithium niobate substrates, even when their P_s value was as small as $P_s \approx 1 \text{ nC/cm}^2$, or when their viscosity was relatively large. The apparent tilt angles θ_{PPLN} of the FLC domains on PPLN substrates agreed with the intrinsic tilt angles θ of the respective FLCs, which were measured in glass cells. This agreement in the measured tilt angles indicates an antiparallel orientation of the spontaneous polarization perpendicular to the substrate in neighbouring FLC domains on PPLN. In the hypothetical case that the periodic poling procedure of lithium niobate fails, it is reasonable to expect that either the periodic domains of the FLC do not appear, or that an apparent tilt angle $\theta_{PPLN} < \theta$ is observed. In the latter case, one can estimate the possible deviation of the direction of the spontaneous polarization from the surface normal by simple geometric considerations, thereby getting more information than only a qualitative assessment of the lithium niobate substrate. After inspection, the cells can be easily disassembled and the cleaned PPLN substrate can be used in further experiments. Owing to its ease and quick execution, this method may provide a valuable tool for non-destructive quality control of PPLN samples, which are very important for the use of non-linear optics.

Authors' statement

The authors of this article contributed to the work as follows. Research concept and design, H.-S.K., H.H., and C.S.; preparation of PPLN substrates, R.R.; collection and assembly of data, P.A.M. and S.K.-B.; data analysis and

interpretation, P.A.M. and H.-S.K.; AFM and EFM measurements, T.R.; writing the article, P.A.M., H.-S.K., and H.H.; critical revision and final approval of article, H.-S.K., H.H., and C.S.

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