Phase-matched second-harmonic generation in a ferroelectric liquid crystal waveguide

Valentina S. U. Fazio\textsuperscript{1,3}, Sven T. Lagerwall\textsuperscript{1}, Philippe Busson\textsuperscript{2}, Anders Hult\textsuperscript{2}, Hubert Motschmann\textsuperscript{3*}

\textsuperscript{1}Department of Microelectronics & Nanoscience, Liquid Crystal Physics, Chalmers University of Technology \& Göteborg University, SE-41296 Göteborg, Sweden
\textsuperscript{2}Department of Polymer Technology, Royal Institute of Technology, SE -10044 Stockholm, Sweden
\textsuperscript{3}Max-Plank-Institute of Colloids and Interfaces, D-14424 Golm/Potsdam, Germany

Abstract
True phase-matched second-harmonic generation in a waveguide of crosslinkable ferroelectric liquid crystals is demonstrated. These materials allow the formation of macroscopically polar structures whose order can be frozen by photopolymerization. Homeotropic alignment was chosen which offers decisive advantages compared to other geometries. All parameters contributing to the conversion efficiency are maximized by deliberately controlling the supramolecular arrangement. The system has the potential to achieve practical level of performances as a frequency doubler for low power laser diodes.

PACS number(s):
61.30.Gd (orientational order of liquid crystals; electric and magnetic field effects on order)
42.65.Tg (optical solitons; nonlinear waveguides)
42.79.Nv (optical frequency converters)

The classical domain of nonlinear optical (NLO) devices based on second-order effects ($\chi^{(2)}$-effects) is frequency doubling which is important for extending the frequency range of laser light sources [1]. The major goals of devices based on third-order nonlinear optical effects ($\chi^{(3)}$-effects) is the realization of optical switches as the decisive hurdle on the way to an all-optical data processing [2]. The design concepts exploit the intensity dependent refractive index due to $\chi^{(3)}$-interactions in Mach-Zehnder type interferometers [3, 4]. Recently it has been demonstrated that an intensity dependent refractive index can also be obtained by a cascading of second order nonlinear processes [5, 6]. This route is far more efficient than the one using $\chi^{(3)}$-effects with currently available materials. As a result, switching occurs at lower intensity levels [7].

The figure of merit of both, frequency doublers and optical switches, is given by the ratio of the susceptibility $\chi^{(2)}$ and refractive index $n$ as $\chi^{(2)}\approx n^2$. Organic materials possess refractive indices $n \approx 1.5$ and thus have an edge to most inorganic materials with refractive index $n \approx 2.2$. Furthermore, organic molecules can be tailored according to the demands and different desired functionalities can be incorporated within a single molecule [8]. The inherent potential has been early recognized and meanwhile there is a sound knowledge of the correlation between molecular structure and corresponding hyperpolarizability, $\beta$ [9, 10].

Organic chromophores possess a remarkably high hyperpolarizability and the major obstacle towards efficient devices is not the availability of suitable chromophores, but the fabrication of proper macroscopic structures.

A high conversion efficiency requires the simultaneous maximization of many parameters and quite often there is a trade-off between some properties. A crucial quantity is $\chi^{(2)}$ which is, subject to certain simplifying assumptions, proportional to the number density of the NLO chromophores and to the orientational average of the hyperpolarizabilities [11]. Hence, a chromophore with high hyperpolarizability should be arranged in a noncentrosymmetric fashion with high number density and high degree of orientational order. To achieve this, mainly two concepts have been pursued so far: Langmuir-Blodgett (LB) films [8, 12] and poled polymers [2]. However, due to intrinsic peculiarities of both techniques, the chromophore is rather diluted and furthermore the films possess limited thermal and mechanical stability. In this study we pursued a different strategy based on ferroelectric liquid crystals (FLCs).

Liquid crystals (LCs) in general form highly ordered phases which possess an intrinsic quadrupolar order but not a dipolar one [13]. Hence for $\chi^{(2)}$ applications conventional LCs are not of any use. However, the picture changed with the advent of FLCs whose molecular symmetry allows a local dipole perpendicular to the director [14]. The arrangement can be manipulated by electric field and huge single domains can be formed. At this stage the orientational order within the monomeric system is still fragile and also sensitive to slight changes in temperature. To overcome these problems the FLCs are further functionalized with photoreactive groups. Subsequent photopolymerization leads to the formation of stable polymer net-

\textsuperscript{*}e-mail: motschma@mpikg-golm.mpg.de
works [15–19] where the polar order is frozen (pyroelectric polymer, PP). Various aspects of the preparation process as well as some nonlinear optical properties are described in a recently submitted publication [19]. In this contribution we focus on the problem of phase-matching in waveguide geometry and demonstrate that true phase-matching is possible to achieve.

The chemical structures of the FLC monomers are shown in Fig. 1. A mixture of 60% A1b and 40% A2c is used which adopts at room temperature a chiral smectic C phase [18]. This mixture is filled in a cell depicted in Figure 2(a) [19]. The bottom plate is equipped with parallel ITO electrodes stripes to achieve a quasi-homeotropic alignment: the smectic layers are aligned parallel to the glass plates, the molecular dipole moments are oriented by the electric field, and the helical structure of the chiral phase is unwound. The mixture of A1b and A2c balances the trade-off between a high polarization on one hand and the field strength required for a manipulation of the helix on the other hand [19]. Even a moderate electric field strength is sufficient to obtain a highly ordered structure and no aligning layers are required. The achieved polar order of the monomeric FLC system is then permanently fixed by photopolymerization leading to a mechanically and thermally stable PP network. Without any additional preparation step this arrangement is also a channel waveguide for TM modes [19]. A linear and nonlinear optical characterization is presented in ref. [19].

According to the prevailing symmetry, second-harmonic generation (SHG) can only occur for TE\(^{\omega}\)–TE\(^{2\omega}\) and TM\(^{\omega}\)–TE\(^{2\omega}\) modes [20]. The measured nonlinear optical constants are remarkably large (up to 1.26 pm V\(^{-1}\)).

Phase-matching can be achieved by taking advantage of the modal dispersion of the waveguide [21]. The effective refractive index \(n_{\text{eff}}\) of a mode is a function of waveguide thickness and polarization. Thus, phase-matching requires the fabrication of a waveguide of a precisely defined thickness given by the linear optical constants. The tolerances are quite tight and already minor deviations within the nanometer range change the characteristics of a device. Also, due to the dispersion of the refractive index, phase-matching is only possible between modes of different order. However, even if this is achieved, the resulting efficiency may still be rather low due to the small value of the overlap integral of the electric field distribution of the interacting modes across the cross-sectional area [21]

\[
\mathcal{I} = \int_0^{\infty} \frac{\chi^{(2)}_{ijk}}{\chi^{(2)}_{\text{eff}}} E_i(m',\omega)(z) E_j(m',\omega)(z) E_k(m,2\omega)(z) \, dz,
\]

where \(\chi^{(2)}_{ijk}\) is the second-order susceptibility tensor, \(\chi^{(2)}_{\text{eff}}\) is the effective second-order susceptibility, and \(E_i(m',\omega)(z)\) is the electric field distribution of the \(m'\)-th mode of frequency \(\omega\) across the waveguide thickness. Field distributions of modes of different order yield a nearly vanishing overlap integral and a poor conversion efficiency [21]. A way out of this dilemma is to influence the susceptibility tensor [22]. A reversal of sign of \(\chi^{(2)}\) at the nodal plane of the electric field distribution of the first-order mode maximizes the value of the overlap integral and thus enables a phase-matching scheme TM\(_0\omega\)–TE\(_1\omega\) and TE\(_0\omega\)–TE\(_1\omega\). The sign of \(\chi^{(2)}\) can be reversed by reversing the polar order of the chromophores.

The desired inverted waveguide structure can be fabricated using the sandwich geometry shown in Figure 2(a). The top plate of a 540 nm thick cell was removed. No damage occurred in this preparation process (the mean roughness is on the order of few nanometers [19] as confirmed by atomic force microscopy). The bottom plate with the polymer network was cut in two pieces of equal size (≈ 4 mm) and the parts were glued onto each other with inverse polarities in the channel region as illustrated in Figure 2(b). Waveguide modes were excited by end-fire coupling. The second-harmonic (SH) light was collected at the end of the guide and measured as a function of the
fundamental light wavelength with a photomultiplier. A quadratic dependence of the SH light intensity on the fundamental one was established to ensure the true nature of the observed signal. The linear constants and the thickness of the waveguide were measured prior to the experiment and used to predict the wavelengths at which phase-matching occurs. According to these data and with a total cell thickness of 2 × 540 nm, TE–TE phase-matching should occur at 958 nm and TM–TE phase-matching at 1311 nm. Indeed, the experiment confirms these predictions: TE–TE phase-matching was observed at 955 nm and TM–TE at 1337 nm, as shown in Figure 3(a).

The width of the peaks in Figure 3(b) and (c) depends on the known dispersion of the refractive indices and on the interaction length $L$ in which fundamental and second harmonic light are in phase. The interaction length can be determined by a fit of the experimental data to the function

$$I_{2\omega} \propto \text{sinc}^2 \left( \frac{L \Delta k}{2} \right),$$

where $\Delta k = 4\pi [n_{\text{eff}}(2\omega) - n_{\text{eff}}(\omega)]/\lambda_\omega$, with $L$ as the only unknown parameter. Figures 3(b) and (c) present the experimental data together with the corresponding fits. The interaction lengths are listed in Table 1. In a sample without $\chi^{(2)}$ inversion the SH signal was about 1000 times smaller than that of an inverted sample at the phase-matching condition, which demonstrated the superior performance due to the optimization of the overlap integral in our geometry. The conversion efficiency

$$\eta = \frac{P_{2\omega}}{P_{\omega}^2 L^2}$$

of the two phase-matching schemes is also given in Table 1. The values are among the largest ones in organic materials. Also, the confinement of TM modes three-dimensionally in the waveguide yields a larger conversion efficiency for TM–TE than for TE–TE phase-matching.

The demonstration of true phase matching in a waveguide format using FLCs is a major step towards a more general use of these materials for NLO devices. FLCs maximize the possible number density of active chromophores and this, together with a high degree of orientation, leads to remarkably high values of the off-resonant nonlinear susceptibilities. Phase-matching was achieved between modes of different order using the modal dispersion of the waveguide. The concept of an inverted structure maximizes the overlap integral and thus enables high efficiency in the desired phase matching-scheme. We have successfully manufactured a macroscopic inverted waveguide and demonstrated phase-matching. The quasi-homeotropic alignment avoids the use of aligning layers and leads to an inherent channel waveguide for TM modes without any additional preparation steps, yielding a very high conversion efficiency for TM–TE phase-matching scheme. Another major feature is that the order of the monomeric FLC is made permanent by photopolymerization. The photopolymerization does not lead to any degradation of the quality of the waveguide, as it is for instance observed in LB films [8]. Apparently the intrinsic fluidity of FLC heals all distortions caused by the formation of new bonds. The polar network is thermally and mechanically stable and all samples kept their NLO properties over the monitored period of several months. Thus, the system has the potential to achieve practical levels of performance.

The authors are grateful to Dr. S. Schrader for helpful discussions and to Prof. H. Möhwald for generous support and encouraging discussions. V. S. U. Fazio and S. T. Lagerwall are grateful to the TMR European Programme (contract number ERBFMNICT983023) and to the Swedish Fundation for Strategic Research for financial support. P. Busson acknowledges the financial support from the Swedish Research Council for Engineering Science (TFR, grant 95-807).

Table 1: Interaction lengths and SH conversion efficiencies for the two phase-matching peaks in Figure 3.

| phase-matched modes | $L$ [mm] | $\eta$ [% W$^{-1}$ cm$^{-2}$] |
|--------------------|---------|-----------------|
| $\text{TE}_0 - \text{TE}_1$ | $0.59 \pm 0.08$ | $0.05 \pm 0.02$ |
| $\text{TM}_0 - \text{TE}_1$ | $0.82 \pm 0.15$ | $0.26 \pm 0.06$ |
References

[1] W. Koechner. Solid state laser engineering. Berlin Springer, 1992.

[2] P. N. Prasad and D. J. Williams. Introduction to nonlinear optical effects in molecules and polymers. John Wiley & Sons, 1991.

[3] D. M. Walba, M. B. Ross, A. A. Clark, R. Shao, K. M. Johnson, M. G. Robinson, J. Y. Liu, and J. Dorowski. Mol. Crys. Liq. Crys., 198:51, 1991.

[4] D. M. Walba, M. B. Ross, A. A. Clark, R. Shao, K. M. Johnson, M. G. Robinson, J. Y. Liu, and J. Dorowski. J. Am. Chem. Soc., 113:5472, 1991.

[5] R. De Salvo, D. J. Hagan, M. Sheik-Bahae, G. I. Stegeman, E. W. Van Stryland, and H. Van Herzeele. Opt. Lett., 17(1):28, 1992.

[6] Y. Baeck, R. Schiek, G. I. Stegeman, G. Assanto, and W. Sohler. Appl. Phys. Lett., 72(26):3405, 1998.

[7] C. Bosshard. Adv. Mater., 8:385, 1996.

[8] A. Ulman. An introduction to ultrathin organic films: from Langmuir-Blodgett to self-assembly. Academic Press Boston, 1991.

[9] S. Hahn, D. Kim, and M. Cho. J. Phys. Chem, 103(39):8221, 1999.

[10] S. Kucharski, R. Janik, and P. Kaats. J. Mater. Chem., 9(2):395, 1999.

[11] H. Motschmann, T. Penner, N. Armstrong, and M. Ezenyilimba. J. Phys. Chem, 97(??):3933, 1993.

[12] M. C. Petty. Langmuir-Blodgett films: an introduction. Cambridge University Press, 1996.

[13] P. G. de Gennes. The physics of liquid crystals. Oxford University Press, 1974.

[14] R. B. Meyer, L. Liebert, L. Strzeleki, and P. Keller. J. Physique, 36:169, 1975.

[15] M. Trollsás, C. Orrenius, F. Salhén, U. W. Gedde, T. Norin, A. Hult, D. Hermann, P. Rudquist, L. Komitov, S. T. Lagerwall, and J. Lindström. J. Am. Chem. Soc., 118:8542, 1996.

[16] M. Trollsás, F. Sahlen, U. W. Gedde, A. Hult, D. Hermann, P. Rudquist, L. Komitov, S. T. Lagerwall, and B. Stebler. Macromol., 29(7):2590, 1996.

[17] D. S. Hermann, P. Rudquist, S. T. Lagerwall, L. Komitov, B. Stebler, M. Lindgren, M. Trollsás, F. Sahlen, A. Hult, U. W. Gedde, C. Orrenius, and T. Norin. Liq. Crys., 24(2):295, 1998.

[18] M. Lindgren, D. S. Hermann, J. Örtergen, P.-O. Arntzen, U. W. Gedde, A. Hult, L. Komitov, S. T. Lagerwall, P. Rudquist, B. Stebler, F. Sahlen, and M. Trollsás. J. Opt. Soc. Am. B, 15(2):914, 1998.

[19] V. S. U. Fazio, S. T. Lagerwall, V. Zauls, S. Schrader, P. Busson, A. Hult, and H. Motschmann. submitted to Phys. Rev. E, 1999.

[20] David Sparre Hermann. Interaction of light with liquid crystals. PhD thesis, Göteborg University and Chalmers University of Technology, 1997.

[21] G. Stegeman and R. Stolen. J. Opt. Soc. Am. B, 6(4):652, 1989.

[22] T. L. Penner, H. R. Motschmann, N. J. Armstrong, M. C. Ezenyilimba, and D. J. Williams. Nature, 367:49, 1994.