

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

Valentina S. U. Fazio<sup>a)</sup> and Sven T. Lagerwall

*Department of Microelectronics and Nanoscience, Liquid Crystal Physics, Chalmers University of Technology and Göteborg University, SE-41296 Göteborg, Sweden*

Philippe Busson and Anders Hult

*Department of Polymer Technology, Royal Institute of Technology, SE-10044 Stockholm, Sweden*

Hubert Motschmann<sup>b)</sup>

*Max-Planck-Institute of Colloids and Interfaces, D-14424 Golm/Potsdam, Germany*

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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. © 2000 American Institute of Physics. [S0003-6951(00)01829-5]

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.<sup>1</sup> 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.<sup>2</sup> The design concepts exploit the intensity dependent refractive index due to  $\chi^{(3)}$ -interactions in Mach-Zehnder type interferometers.<sup>3,4</sup> Recently it has been demonstrated that an intensity dependent refractive index can also be obtained by a cascading of second-order nonlinear processes.<sup>5,6</sup> 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.<sup>7</sup>

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  $\chi^{(2)2}/n^3$ . 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.<sup>8</sup> The inherent potential has been early recognized and meanwhile there is a sound knowledge of the correlation between molecular structure and corresponding hyperpolarizability,  $\beta$ .<sup>9,10</sup> 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.<sup>11</sup> 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<sup>8,12</sup> and poled polymers.<sup>2</sup> 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.<sup>13</sup> 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.<sup>14</sup> 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 polymerizable groups. Subsequent photopolymerization leads to the formation of stable polymer networks<sup>15-19</sup> 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.<sup>19</sup> 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.<sup>18</sup> This mixture is filled in a cell depicted in Fig. 2(a).<sup>19</sup>

<sup>a)</sup>Electronic mail: fazio@fy.chalmers.se

<sup>b)</sup>Electronic mail: motschma@mpikg-golm.mpg.de

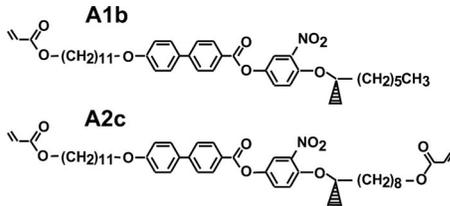


FIG. 1. FLC monomers used in this experiment.

The bottom plate is equipped with parallel indium tin oxide (ITO) electrodes stripes to achieve a quasihomotropic 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.<sup>19</sup> 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 transverse magnetic (TM) modes.<sup>19</sup> A linear and nonlinear optical characterization is presented in Ref. 19 (absorption, scattering losses, second-order reduced nonlinear optical susceptibilities). According to the prevailing symmetry, second-harmonic generation can only occur for transverse electric  $TE^\omega-TE^{2\omega}$  and  $TM^\omega-TE^{2\omega}$  modes.<sup>20</sup> The measured nonlinear optical constants are remarkably large (up to  $1.26 \text{ pm V}^{-1}$ ).

Phase-matching can be achieved by taking advantage of the modal dispersion of the waveguide.<sup>21</sup> 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<sup>21</sup>

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

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.<sup>21</sup> A way out of this dilemma is to influence the susceptibility tensor.<sup>22</sup> 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  $TM_0^\omega-TE_1^{2\omega}$  and  $TE_0^\omega-TE_1^{2\omega}$ . 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 Fig. 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<sup>19</sup> as confirmed by atomic force microscopy). The bottom plate with the polymer network was cut in two pieces of equal size ( $\approx 4 \text{ mm}$ ) and the parts were glued onto each other with inverse polarities in the channel region as illustrated in Fig. 2(b).<sup>23</sup> 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  $2 \times 540 \text{ nm}$ , 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 Fig. 3(a).

The width of the peaks in Figs. 3(b) and 3(c) depends on the known dispersion of the refractive indices and on the interaction length  $L$  in which fundamental and SH 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 3(c) present the experimental data together with the corresponding fits. The interaction lengths are listed in Table I. 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 normalized conversion efficiency

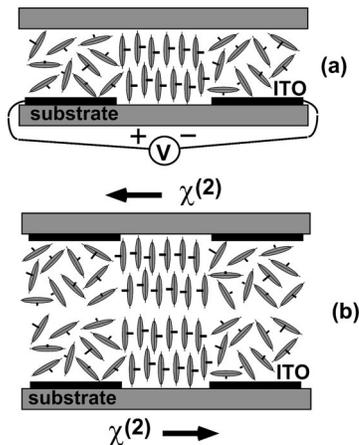


FIG. 2. (a) Cross section of a cell. Cell thickness is 540 nm. Electrode distance is  $100 \mu\text{m}$ . (b) Scheme of the  $\chi^{(2)}$ -inverted structure.  $\chi^{(2)}$  undergoes an abrupt sign reversal at half the total thickness of the cell. Cell thickness is  $2 \times 540 \text{ nm}$ .

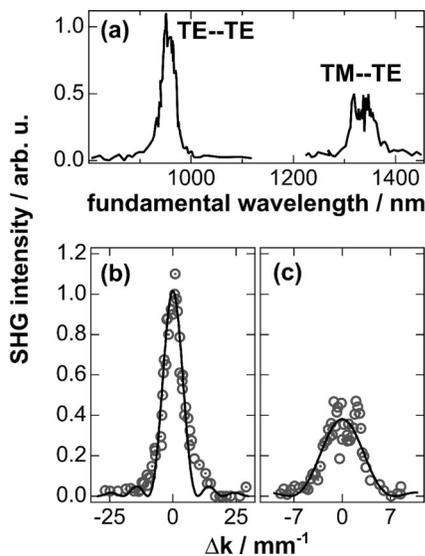


FIG. 3. (a) Phase-matching peaks as a function of the fundamental light wavelength. (b)  $\text{TE}_0^\omega - \text{TE}_1^{2\omega}$  phase-matching peak at 955 nm, data and fit. (c)  $\text{TM}_0^\omega - \text{TE}_1^{2\omega}$  phase-matching peak at 1337 nm, data and fit. The laser source was a tunable OPG/OPA system pumped by the third harmonic of a Nd-yttrium-aluminum-garnet laser (energy per pulse  $\sim 30$  mJ, pulse duration 35 ps).

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

of the two phase-matching schemes is also given in Table I. 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. Applying the concept of an inverted structure<sup>22</sup> 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 quasihomotropic 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 normalized conversion efficiency for TM-TE phase-matching scheme. Another major feature is that the order of the monomeric FLC is

TABLE I. Interaction lengths and normalized SH conversion efficiencies for the two phase-matching peaks in Fig. 3.

Phase-matched modes	$L$ (mm)	$\eta$ (% $\text{W}^{-1} \text{cm}^{-2}$ )
$\text{TE}_0^\omega - \text{TE}_1^{2\omega}$	$0.59 \pm 0.08$	$0.05 \pm 0.02$
$\text{TM}_0^\omega - \text{TE}_1^{2\omega}$	$0.82 \pm 0.15$	$0.26 \pm 0.06$

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.<sup>8</sup> 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.

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- <sup>23</sup>The sandwich cell was assembled in a polarizing microscope, where the ITO boundaries are visible and it is easy to precisely align the two half cells.