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Significant Enhancement of the Optical Second Harmonic Generation in a Poled Azopolymer Thin Grating

F. Lagugné-Labarthet,* F. Adamietz, V. Rodriguez, and C. Sourisseau

Laboratoire de Physico-Chimie Moléculaire, UMR 5803 CNRS, Université Bordeaux 1, 351 Cours de la Libération, 33405 Talence Cedex, France

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Nonlinear optical properties of an electrically poled surface relief grating inscribed on a thin film of azopolymer have been investigated. The linear and nonlinear optical far-field diffraction patterns of the grating are compared, and they show a clear angular separation of the fundamental ($\lambda = 1.064\ \mu$m) and second harmonic generated beams that are diffracted at different angles. The intensity of the zero order transmitted second harmonic generation (SHG) beam from inscribed surface relief grating (SRG) areas has been recorded using the Maker fringe technique and compared to the response from flat areas that were only poled. Poled gratings exhibit a sharp second harmonic generation enhancement for coupling angles of $\theta_i = \pm 52°$ due to a quasi-phase matching process. A simple phenomenological model allows one to explain both the second harmonic intensity generated from the thin polar film and the dispersion curve observed under "pp" polarization due to the mismatch of the angular coupling condition: this gives us a good indication of the intensity enhancement of the SHG beam in the forward direction.

1. Introduction

Nonlinear optical gratings are materials organized at the mesoscale and are of major interest in the field of photonics.[1,2] Periodically poled gratings inscribed on lithium niobate or KTP crystals are, for instance, currently used in many applications, such as optical parametric oscillators, second harmonic and difference frequency conversion units. These gratings are usually designed to work in the infrared range, with their periodicity varying in the range 10−30 μm; they are built using a multistep lithography procedure together with an intense electric field to induce permanent and periodic modifications in their nonlinear responses. Such nonlinear gratings can also be inscribed on polymer materials that contain azobenzene chromophores with high hyperpolarizabilities.[3−7] This alternative has stimulated a lot of interest, since the processing of thin polymer films is actually easier, and it offers a better flexibility to design planar waveguides and diffractive elements despite intrinsic absorption losses in the polymers.[8] Azobenzene-containing polymers are indeed very good candidates, and they are unique materials, in which it is first possible to inscribe surface relief grating (SRG) with high efficiency and good stability and, second, the poled films may display an intrinsic high $\chi^{(2)}_{zzz}$ susceptibility when they are oriented in a noncentrosymmetric arrangement.[9,10] In a previous study, we investigated the local properties of such azobenzene based gratings by combining micro-Raman confocal measurements and second harmonic generation (SHG) measurements in near-field optical scanning microscopy to estimate the order parameters and the chromophore orientation distribution functions in the different regions of a DC poled grating.[10] Far-field second order nonlinear diffraction measurements were also carried out, and the relative intensities of the diffracted orders were related to the peculiar half-periodic second order $\chi^{(2)}$ variations along the grating $\vec{k}$ vector.[11]

In this letter, we report an investigation of the far-field linear and nonlinear diffraction properties of a poled thin grating. In fact, the idea of using a grating as a coupler for efficient excitation of a linear optical guided wave in thin films was originally proposed by Dakss et al.[12] and later extended to second order nonlinear effects by Che et al.[1,3] Thus, we have first recorded and compared the linear and nonlinear transmitted diffracted orders of a grating inscribed on a homopolymer film functionalized with azobenzene side-chain chromophores. In a second set of experiments, we have used the Maker fringe technique to compare the SHG intensities transmitted by the poled film (i) from areas where a SRG was inscribed and (ii) from areas without grating. The poled grating areas exhibit an additional strong and sharp peak corresponding to quasi-phase matching conditions at a coupling angle where a very high efficiency in SHG is actually occurring.

2. Materials and Methods

Nonlinear Grating Inscription. Using a holographic scheme, we have first inscribed a SRG on an azopolymer thin film (thickness = 410 nm). The grating has a periodicity of 1.37 μm and a surface relief amplitude of ~400 nm. Experimental details can be found elsewhere.[9−11,13] In fact, to induce a noncentrosymmetry in the azobenzene chromophore orientations, a 4 kV dc electric field was applied over the thin grating at a temperature of 90 °C, which is ~30 °C below the glass transition of the polymer. Such high-field poling conditions were conducted using a wire poling scheme with a tungsten wire (25 μm diameter) held 5 mm above the thin film and oriented

* Corresponding author. E-mail: f.lagugne@lpcm.u-bordeaux1.fr.

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perpendicular to the grating grooves. The film was then cooled to room temperature keeping the dc field on. Repeated measurements of the SHG Maker fringes indicated a good stability of the nonlinear optical response over a long time period; a sample kept under dark conditions for several years (>4 years) showed an efficiency as large as d_{33} = 200 pm/V at 1064 nm (ref. αQuartz with d_{11} = 0.3 pm/V).

Second Harmonic Diffraction Measurements. Using a Q-switched Nd:YAG pulsed laser operating at $\lambda_\omega = 1.064$ μm with a 30 Hz repetition rate and an energy density of ~2μJ/cm^2 at the sample, the diffraction pattern was measured in the transmission mode with the help of a photomultiplier tube (PMT, Hamamatsu H6779-01 type) mounted on a goniometer allowing a 0.5° step scan resolution. For the optical linear diffraction measurements, we have made use of a filter to cut the SH light coming into the PMT while a band-pass filter (fwhm = 10 nm) was used to suppress the input wavelength and measure the second harmonic light ($\lambda_{2\omega}$ = 532 nm).

3. Results and Discussion

In a first set of experiments, we have measured the linear and nonlinear diffraction patterns at incidence angles of θ_i = 0° and θ_i = 50°. At normal incidence (θ_i = 0°, Figure 1a), the linear pattern measured with a p polarized (horizontal) 1064 nm beam displays the transmitted 0th order and first ±1 orders at the diffraction angles $\theta_d^{\pm1}(\omega) \cong \pm 50°$. The diffraction efficiency at 1064 nm was estimated to about 11%. Similarly, the nonlinear pattern measured at 532 nm shows the first diffracted orders at $\theta_d^{\pm1}(2\omega) \cong \pm 22°$ and the second orders at $\theta_d^{\pm2}(2\omega) \cong \pm 50°$, which obviously coincide with $\theta_d^{\pm1}(\omega)$. It is noteworthy that no SHG was observed in the forward direction, since the major susceptibility tensor element $\chi_{zzz}^{(2)} = 2d_{33}$ is along the propagation direction of the fundamental beam.

Similarly, the nonlinear patterns measured at θ_i = 50° are shown in Figure 1b and both transmitted 0th orders are now observed with a strong intensity at $\theta_d \cong -50°$ relative to the normal of the grating surface. In Figure 1b, several diffracted SH orders are detected at $\theta_d^{+1}(2\omega) \cong -25°$, $\theta_d^{+2}(2\omega) \cong -3°$, and $\theta_d^{+3}(2\omega) \cong +20°$, respectively; the +4th diffracted order is normally expected at about $\theta_d^{+4}(2\omega) \cong +52°$ (Figure 1c). Thus, whatever the incidence angle is, the diffraction angle of the various m orders is varying according to the general diffraction law: $\sin\theta_d = [(m\lambda/\Lambda) - \sin\theta_i]$. The corresponding simulated expectations are gathered in Figure 1c for a grating spacing of Λ = 1.37 μm.

The angular separation of the fundamental input beam and SHG diffracted signals is clearly evidenced in Figure 1; in particular, the ±1st SHG diffracted orders are well separated from any contribution of the fundamental beam. Two essential functions are thus highlighted in such an optical device: they combine simultaneously (i) spatial filtering of 2ω and (ii) efficient second harmonic generation from the thin poled polymer film.

To reveal the nonlinear optical properties of the polar grating, we have investigated the intensity variations of the SH beam in the transmission mode direction using the Maker fringe procedure.[14] The intensity of the SH beam was measured for various angles of incidence of the fundamental beam with both polarization combinations set to "pp" and "sp", where the first term is the input polarization and the second term the polarization direction of the analyzer. The symbols p and s stand for the in-plane (horizontal) and out-of-plane (vertical) directions with respect to the plane of incidence, with the horizontal

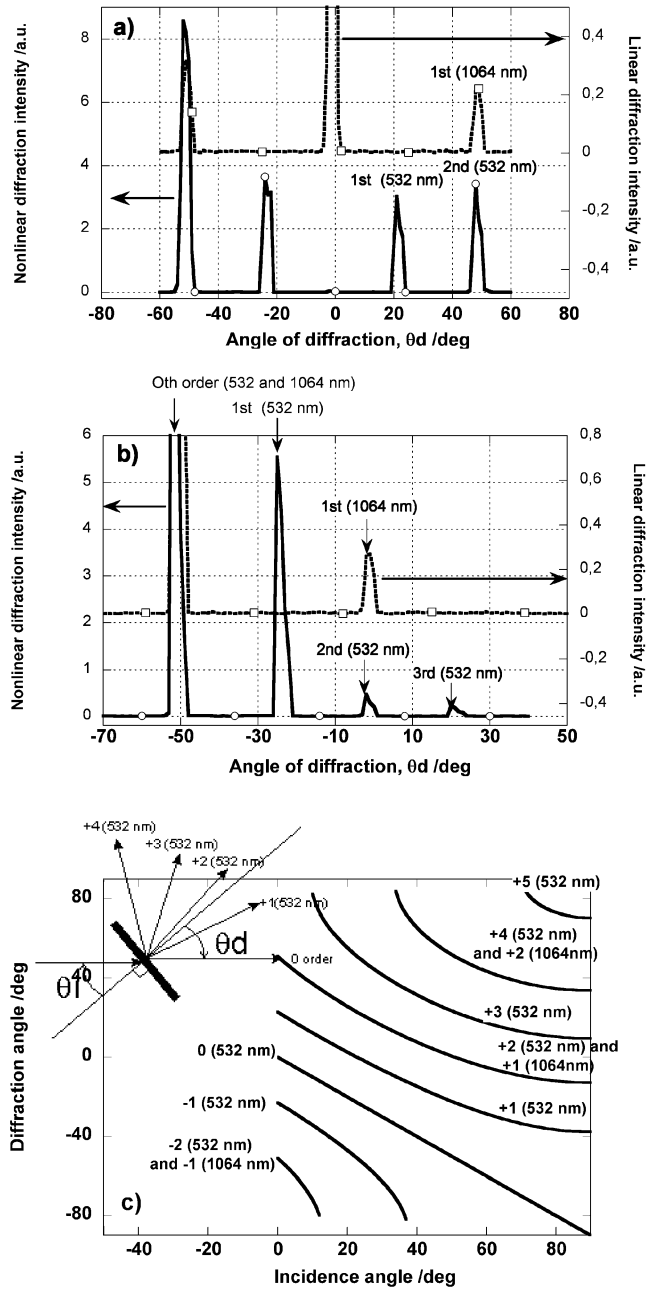

Figure 1. Linear (1064 nm) and nonlinear second harmonic (532 nm) experimental diffraction patterns measured in the transmission mode from an electrically poled grating with a period spacing of 1.37 μm at an incidence angle of (a) 0° and (b) 50°, respectively. (c) Diffraction angles versus angle of incidence for a grating with a periodicity of 1.37 μm and for wavelengths of 1064 and 532 nm.

coinciding with the grating $\vec{k}$ vector. Using the same thin film sample, we have thus measured and compared the Maker fringe patterns on areas where a grating was inscribed and on grating-free areas (Figure 2). For the "pp" polarization configuration, in areas free of SRG, the Maker fringe pattern shows a broad maximum at $\theta_i \cong \pm 55°$ and a minimum at normal incidence (θ_i = 0°). As shown in Figure 2, it is noteworthy that the "pp" response is larger than the "sp" one; the ratio $(I_{SP}/I_{PP})^{1/2}$ is significantly weaker than 0.33, confirming that the poling has actually been realized under high-field conditions.[15-17] The complete treatment of the whole SHG polarized data following a published procedure leads to large values of the d_{33} nonlinear optical coefficient equal to about 200 pm/V in the flat areas.[9,10] More interestingly, similar polarized recordings on the poled grating exhibit at the incidence angles of about ±52° an intense

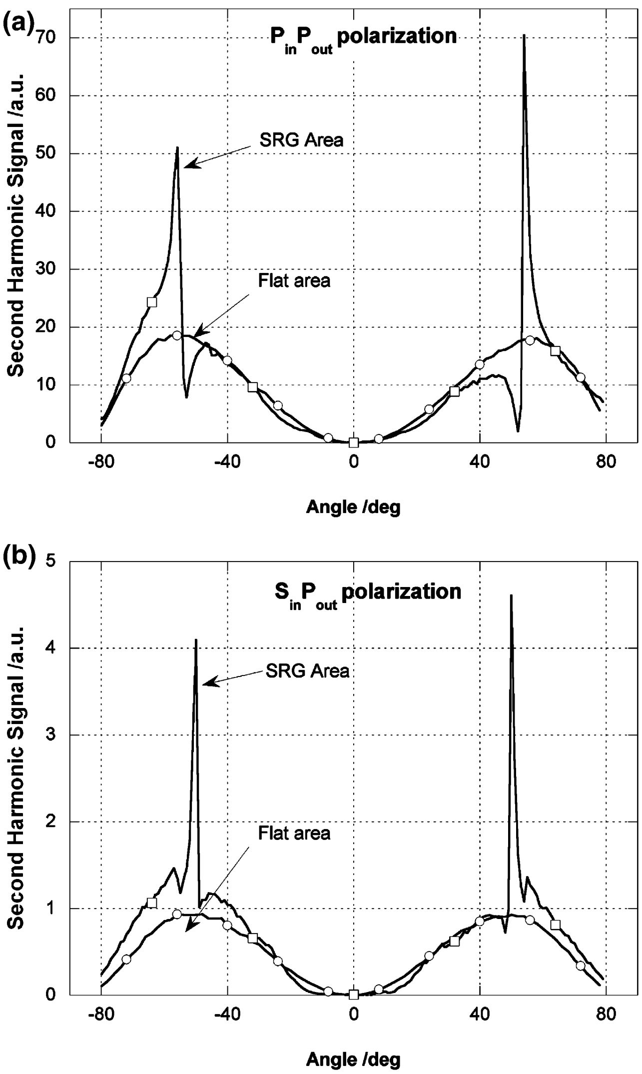

Figure 2. Maker fringes measured for a poled thin film (○) on flat areas and (□) on regions where a surface relief grating was inscribed, using (a) "pp" and (b) "sp" polarization combinations, respectively.

dispersion-like sharp curve, which is superimposed on a broad Maker fringe envelope, as previously observed on the flat film area. The SH intensity maximum is now enhanced by a factor equal to ∼3−4, as compared to the response in flat regions:[18] this denotes a significant energy conversion in that direction and a strong efficiency in the light frequency doubling.

For the "sp" polarization combination, a similar sharp peak and enhancement is observed at a slightly smaller angle of $\theta_i \cong \pm 50°$. This angular shift is presumably due to the large birefringence within the thickness of the thin film and/or to the induced anisotropy in the chromophore orientations by the poling effect.[9,10] Also, additional effects due to the geometry of the grating and possible differences in the transmission responses of "s" and "p" polarized light are probably perturbing the shape of the enhanced curve at the coupling angles, as shown in Figure 2.

The existence of these new SH responses can be rationalized by considering the involved laws of momentum conservation. First, at a linear optical level, the guiding conditions of light in such a multilayered diffracting structure imply[1,3,12]

$$\vec{k}^{\omega}_{\text{incident}} + \vec{k}^{\omega}_{\text{guided}} = \vec{k}^{\omega}_{\text{diffracted}} \tag{1}$$

where

$$|k_{\text{incident}}| = \frac{2\pi}{\lambda_\omega}\sin\theta_i, \quad |k_{\text{guided}}| = \frac{2\pi}{\lambda_\omega}N_{\text{eff}}, \quad \text{and } |k_{\text{diffracted}}| = \frac{2m\pi}{\lambda_\omega}\sin\theta_d \tag{2}$$

From eq 1, using $\theta_i = \theta_d$ for the transmitted 0th order, the relation between the effective refractive index and the coupling angle leads to the expression already proposed by Che et al.:[1,3]

$$\sin\theta_i + N_{\text{eff}} = \pm m\frac{\lambda_i}{\Lambda} \tag{3}$$

Second, at the nonlinear optical level, the diffraction phase matching condition implies

$$\vec{k}^{\omega}_{\text{diffracted}} + \vec{k}^{\omega}_{\text{diffracted}} = \vec{k}^{2\omega}_{\text{diffracted}} \tag{4}$$

When the condition of perfect phase matching is fulfilled, that is, all the SHG is efficiently transmitted and no guided wave is induced, from eq 3 with $\lambda_i = 1.064$ μm, $\Lambda = 1.37$ μm, and $m = +1$, one finds $\theta_i = +52°$, which is in very good agreement with the position of SH enhancement discussed above in Figure 2. This angle corresponds as well to that of the diffracted second order ($m = \pm 2$) for the SHG wave at 532 nm. With the surface relief of the thin grating being regular along the grating vector, we do observe the same resonant or coupling angle when the grating is tilted at $\theta_i = -52°$.

Since the grating has an intrinsic second order nonlinearity, the superimposition of both the first diffracted order at 1064 nm and the second diffracted order at 532 nm is thus an essential condition to enhance the SH signal; this is due to a "quasi"-phase matching at the coupling angle $\theta_{\text{coupling}} = \pm 52°$. Obviously, in SHG transmission experiments, all of these phenomena will exist simultaneously with the classical Maker fringe interferences, which are governed by the phase matching rule, $|\Delta k| \cong 0$, involving the following averaged quantities:

$$|\Delta k| = |\langle\vec{k}_{2\omega}\rangle - \langle 2\vec{k}_{\omega}\rangle| = \frac{4\pi}{\lambda_\omega}[\langle n_{2\omega}\rangle\cos\theta_{2\omega} - \langle n_\omega\rangle\cos\theta_\omega] \tag{5}$$

where $\langle n_{2\omega}\rangle = 1.950$, $\langle n_\omega\rangle = 1.768$, and $\theta_{2\omega}$ and θ_ω are the corresponding incidence angles in the thin film.[9]

Extensive calculations considering the Fresnel, absorption, and anisotropy coefficients for a variety of layered samples have been recently developed for the analyses of Maker fringe experiments, and powerful methods based on matrix formulation have shown an excellent agreement between theory and experiment for different polarization configurations.[15,17,19−21] For instance, examples of successful analyses performed on poled azopolymer samples with strong optical anisotropy and absorption have recently been published.[9,10] However, in the present study, it is not straightforward to apply a similar formalism, since new phase relations between the transmitted and diffracted beams at ω and 2ω are effective because of the grating properties. Actually, since we are dealing with very thin films, it is reasonable to assume that the curves shown in Figure 2 stem from the superimposition of two functions: the first one is related to an envelope term which is characteristic of the Maker fringe pattern, and the other one is due to a sharp function centered at the coupling angle.

In the simple case of an homogeneous isotropic thin film, such as the flat areas under study, the transmitted second

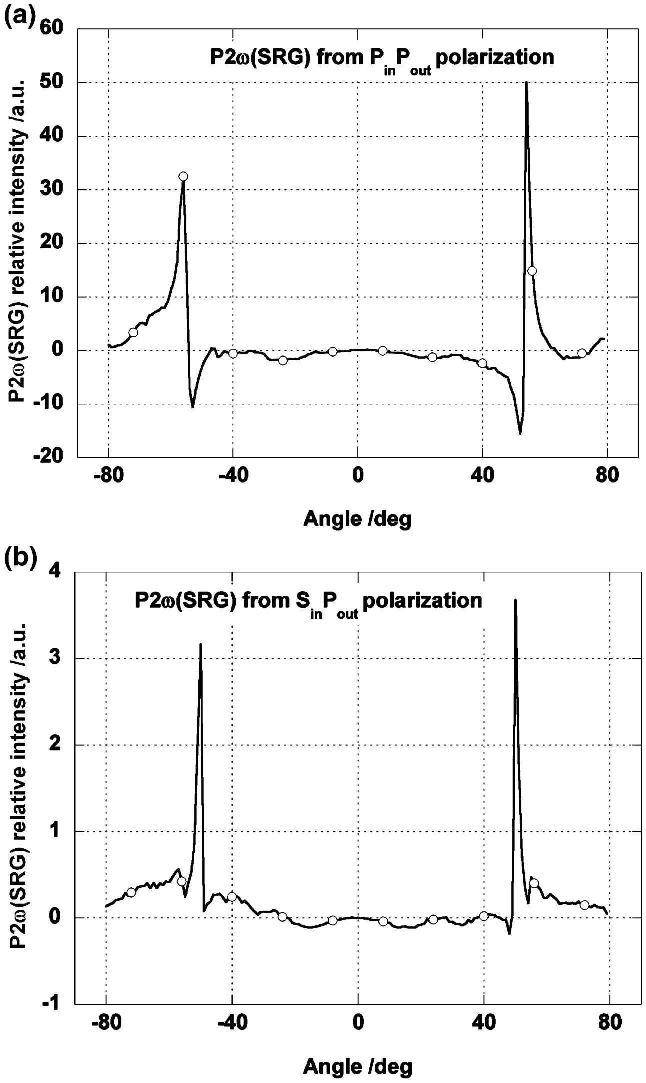

Figure 3. Comparison of the experimental difference curves of the transmitted SHG signal due to the SRG diffraction contribution for poled grating areas for (a) "pp" polarization and (b) "sp" polarization.

harmonic power can be qualitatively given by

$$P_{2\omega}^{\text{FlatArea}} = \frac{512\pi^3}{A} P_{\omega}{}^2 \frac{(t_{\text{af}})^4 (t_{\text{fs}})^2 (t_{\text{sa}})^2}{n_{2\omega}{}^2 \cos^2 \theta_{2\omega}} \left(\frac{2\pi L}{\lambda}\right)^2 d_{\text{eff}}{}^2 \frac{\sin^2(L\Delta k/2)}{(L\Delta k/2)^2} \tag{6}$$

where A is the beam area, P_ω is the incident power, t_{ij} are the Fresnel transmission coefficients, L is the film thickness (which is actually smaller than the coherence length), d_{eff} is the effective susceptibility, and Δk is the phase mismatch as defined above.

Then, to extract the additional enhanced signal from SRG areas, we have subtracted a broad SH envelope due to the flat area from the experimentally observed total SHG signal and, for simplicity, we assume this difference is due to the contribution of the SR grating, that is,

$$P_{2\omega}^{\text{Total}}(\theta_{\text{i}}) - P_{2\omega}^{\text{FlatArea}} = P_{2\omega}^{\text{SRGrating}} \tag{7}$$

As shown in Figure 3a, for the "pp" configuration, a dispersion line shape function is thus obtained, peaking at a maximum angle of ±54°, that is, with an angular shift of ±4° with respect to the Maker fringe maxima. Such a response can be simulated by using the following simple dispersion line shape:

$$P_{2\omega}^{\text{SRGrating}} = C \frac{(\theta_{\text{i}} - \theta_{\text{coupling}})\tau^2}{1 + (\theta_{\text{i}} - \theta_{\text{coupling}})^2 \tau^2} \tag{8}$$

where C is an amplitude factor, θ_{i} is the incidence angle on the nonlinear grating, θ_{coupling} is the optimum incidence angle for phase matching (eq 5), and $\tau = 1/\Delta\theta$ is the angular mismatch; that is, $2\Delta\theta$ represents the peak-to-peak angular separation. In this case, a reasonable fit can be obtained using $\theta_{\text{coupling}} = \pm 52°$, $\Delta\theta = 0.085°$ (0.015 rad), and an amplitude factor of $C \approx 3.0$. Even though it is difficult to accurately estimate the relative amplitudes under this simple approach, an enhancement SHG factor of about 2.4−3.7 seems effective in the near vicinity of the coupling angle.

More importantly, the dispersion curve shows clearly a decreasing contribution for $\theta_{\text{i}} < \theta_{\text{coupling}}$ and a phase lag between the radiated SH and diffracted SH beams is occurring; conversely, for $\theta_{\text{i}} > \theta_{\text{coupling}}$, the phase shift is positive and leads to an increasing amplitude: we are thus dealing with a new optical device behaving as a drastic SH enhancement at a peculiar coupling angle. Also, it is noteworthy that we have performed simulations for different values of $\Delta\theta$ varying from 0.015 rad (0.85°) to 0.1 rad (5°). For a large angular mismatch (i.e., $\theta_{\text{i}} \neq \theta_{\text{coupling}}$), there was a very weak dispersion amplitude that could not be accounted for in the resulting simulated curves.

In contrast, as shown in Figure 3b, for the "sp" polarization condition, the situation is slightly different, since in areas containing the poled SR grating we do observe a delta shape intense signal peaking at ±50°, that is, in exact coincidence with respect to the Maker fringe maxima. Perfect enhancement conditions seem fulfilled, and the SHG amplification factor is now equal to 3.3−4.0.

Finally, all of the above results demonstrate that such poled surface relief gratings have interesting new nonlinear optical properties but, to achieve a drastic and efficient SHG enhancement, a very high accuracy in the coupling angle (resolution <1°) will be necessary in any potential applications.

4. Conclusion

A drastic enhancement of SHG from a poled surface relief grating inscribed on an azobenzene-containing polymer thin film has been observed when the phase and the angular matching conditions are fulfilled. In this present study of a grating with a 1.37 μm period, a sharp SH additional peak is observed at a coupling angle with a 3−4-fold intensity increase as compared to the maximum value emitted by the same poled thin film without grating inscription. Since a flat poled film of functionalized azobenzene polymer has an intrinsic nonlinear coefficient of $d_{33} \cong 200$ pm/V, the inscription of a SRG represents a significant improvement in the SHG efficiency. Although more theoretical investigations are required to better evaluate the phase interferences between the fundamental and the second harmonic diffracted beams by the modulated surface relief structure, we have shown that a simple qualitative approach can be proposed and it explains nicely the superimposition of the Maker fringe patterns with a locally and markedly enhanced second harmonic signal at a peculiar coupling angle.

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