Suppression of nonlinear optical signals in finite interaction volumes of bulk materials

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Abstract: We show that nonlinear optical signals generated by non-phase-matched interactions are strongly suppressed when the interaction volume is finite and localized deep inside the bulk of a homogeneous material, as opposed to the case where the interaction volume extends across a boundary of the material. The suppression in the bulk originates from destructive interference between the signals generated in the two regions where the interaction is gradually turned on and off and depends on the ratio of the coherence length to the characteristic length of the interaction volume.

OCIS codes: (190.4350) Nonlinear optics at surfaces; (310.6860) Thin films, optical properties.

References

1. R. W. Boyd, *Nonlinear Optics* (Academic, San Diego, 1992).
2. P. Günter, ed., *Nonlinear Optical Effects and Materials* (Springer, Berlin, 2000).
3. T. F. Heinz, "Second-order nonlinear optical effects at surfaces and interfaces," in *Nonlinear Surface Electromagnetic Phenomena*, H.–E. Ponath and G. I. Stegeman, eds. (Elsevier, Amsterdam, 1991), pp. 353-416.
4. J. A. Giordmaine, "Nonlinear optical properties of liquids," Phys. Rev. **138**, A1599-A1606 (1965).
5. P. M. Rentzepis, J. A. Giordmaine, and K. W. Wecht, "Coherent optical mixing in optically active liquids," Phys. Rev. Lett. **16**, 792-794 (1966).
6. A. P. Shkurinov, A. V. Dubrovskii, and N. I. Koroteev, "Second harmonic generation in an optically active liquid: Experimental observation of a fourth-order optical nonlinearity due to molecular chirality," Phys. Rev. Lett. **70**, 1085-1088 (1993).
7. P. Fischer, D. S. Wiersma, R. Righini, B. Champagne, and A. D. Buckingham, "Three-wave mixing in chiral liquids," Phys. Rev. Lett. **85**, 4253-4256 (2000).
8. M. A. Belkin, T. A. Kulakov, K.-H. Ernst, L. Yan, and Y. R. Shen, "Sum-frequency vibrational spectroscopy on chiral liquids: A novel technique to probe molecular chirality," Phys. Rev. Lett. **85**, 4474-4477 (2000).
9. M. A. Belkin, S. H. Han, X. Wei, and Y. R. Shen, "Sum-frequency generation in chiral liquids near electronic resonance," Phys. Rev. Lett. **87**, 113001 (2001).
10. G. Berkovic, Y. R. Shen, G. Marowsky, and R. Steinhoff, "Interference between second-harmonic generation from a substrate and from an adsorbate layer," J. Opt. Soc. Am. B **6**, 205-208 (1989).
11. S. Cattaneo and M. Kauranen, "Determination of second-order susceptibility components of thin films by two-beam second-harmonic generation," Opt. Lett. **28**, 1445-1447 (2003).
12. S. Cattaneo and M. Kauranen, "Polarization-based identification of bulk contributions in surface nonlinear optics," Phys. Rev. B **72**, 033412 (2005).
13. S. Cattaneo, "Two-beam surface second-harmonic generation," Ph.D. thesis, Tampere University of Technology, Tampere, Finland, 2004.
14. P. Figliozzi, L. Sun, Y. Jiang, N. Matlis, B. Mattern, M. C. Downer, S. P. Withrow, C. W. White, W. L. Mochán, and B. S. Mendoza, "Single-beam and enhanced two-beam second-harmonic generation from silicon nanocrystals by use of spatially inhomogeneous femtosecond pulses," Phys. Rev. Lett. **94**, 047401 (2005).
15. L. Sun, P. Figliozzi, Y. Q. An, and M. C. Downer, "Nonresonant quadrupolar SHG in isotropic solids using two orthogonally polarized laser beams," Opt. Lett., in press.
16. J. E. Sipe, "New green-function formalism for surface optics ," J. Opt. Soc. Am. B **4**, 481-489 (1987).
17. P. Guyot-Sionnest, W. Chen, and Y. R. Shen, "General considerations on optical second-harmonic generation from surfaces and interfaces," Phys. Rev. B **33**, 8254–8263 (1986).
18. J. E. Sipe, V. Mizrahi, and G. I. Stegeman, "Fundamental difficulty in the use of second-harmonic generation as a strictly surface probe," Phys. Rev. B **35**, 9091–9094 (1987).

#8686 - $15.00 USD Received 6 September 2005; revised 10 November 2005; accepted 13 November 2005

19. P. Guyot-Sionnest and Y. R. Shen, "Bulk contribution in surface second-harmonic generation," Phys. Rev. B **38**, 7985-7989 (1988).
20. Y. R. Shen, "Surface contribution versus bulk contribution in surface nonlinear optical spectroscopy," Appl. Phys. B **68**, 295-300 (1999).

1. Introduction

Second-order nonlinear optical processes have applications in frequency conversion of light [1], optical signal processing [2], and in the characterization of surfaces and thin films [3]. Two fundamental issues are associated with such processes. First, second-order processes are only allowed in noncentrosymmetric materials [1]. Therefore, anisotropic materials with polar order are usually needed to take advantage of the processes. Second, the interaction needs to be phase-matched, i.e., a phase relation between the interacting fields needs to be maintained through the length of the nonlinear material [1].

The centrosymmetry rule is strictly valid within the electric-dipole approximation of the light-matter interaction [1]. Nonlinear processes involving higher multipole (in particular, magnetic-dipole and electric-quadrupole) interactions, on the other hand, are allowed also in centrosymmetric materials. This is of particular interest as such effects give rise to a second-order response also in materials with high macroscopic symmetry, including isotropic materials with no polar order.

Isotropic materials can also give rise to an electric-dipole-allowed second-order response if the material is chiral [4-9]. In such materials, however, only sum- and difference-frequency generation is allowed, whereas second-harmonic generation is forbidden. While early reports on these effects [5,6] stated that they are easily observable, more recent reports suggest that they are observable only under favorable near-resonant conditions [7-9]. The conflicting results lead to a discrepancy of several orders of magnitude regarding the nonlinearity of the material.

A common feature of the electric-dipole-allowed and the higher-multipolar second-order response of isotropic materials is that they can only be accessed using two noncollinear input beams and proper polarization combinations [3,4]. The use of noncollinear input beams has two important consequences. First, the interaction has a very large phase mismatch even in an ideal nondispersive medium, which makes phase matching extremely difficult to achieve in real materials [1]. Second, the interaction volume will in practice be limited by the overlap of beams of finite transverse size.

In this paper, we show that phase mismatch leads to a strong suppression of the generated nonlinear signals when the interaction volume is finite and localized deep in the bulk of the nonlinear material. On the contrary, localization near the boundary of the material is more favorable. Compared to the signal intensity obtained near the boundary, the suppression of the signal deep in the bulk is on the order of $(l_c/L)^2$, where l_c is the coherence length of the nonlinear interaction and L is the length of the interaction volume. We emphasize that the effect is not related to the surface nonlinearity of the material. Even in the proximity of the boundary, the nonlinear response originates from the bulk and the differences arise from phase matching considerations.

2. Theoretical description

To describe the effect, we consider the situation where two noncollinear input beams at frequencies ω_1 and ω_2 (same or different) are applied on a material with a second-order nonlinear response and occupying the region $0 \le z \le d$ (Fig. 1). The fundamental beams are of finite transverse size but otherwise collimated and plane-wave-like with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$. The nonlinear response to the input beams gives rise to a nonlinear polarization at frequency $\omega_3 = \omega_1 + \omega_2$, which acts as a source for the generation of a new beam at ω_3 with wave vector $\mathbf{k}_3$. The interaction is then characterized by the phase mismatch $\Delta\mathbf{k} \equiv \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$ [1], which we take to be along the *z* direction ($\Delta\mathbf{k} = \Delta k\ \hat{\mathbf{z}}$).

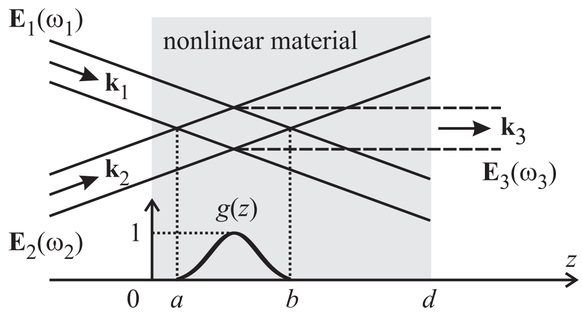

Fig. 1. Schematic diagram of noncollinear three-wave mixing. Two plane-wave-like input beams of finite transverse size intersect in a nonlinear medium occupying the region $0 \le z \le d$. The function $g(z)$ describes the variation in the strength of the source polarization due to the overlap of the input beams. $g(z)$ is expected to be a smooth, real function that grows from zero to the maximum and then decreases back to zero over the interval $a < z < b$.

The generated field amplitude at ω_3 can be calculated by inserting the source polarization into the nonlinear wave equation and integrating over space. For infinite plane waves and undepleted input beams, the amplitude exiting the nonlinear medium is proportional to the integral [1]

$$\int_0^d e^{i\Delta kz} dz = \frac{1}{i\Delta k}\left(e^{i\Delta kd} - 1\right) . \tag{1}$$

This leads to the familiar oscillating behavior (Maker fringes) of the field amplitude as a function of *d*, with the coherence length $l_c = \pi/\Delta k$.

In the present case of intersecting beams of finite size, however, the source polarization needs to be weighed by a function $g(z)$, which describes the overlap of the input beams. $g(z)$ need not be specified in detail but is expected to be a smooth, real function, which grows from zero to the maximum value of unity and then decreases back to zero over the interval $a < z < b$ (Fig. 1). In several practical situations, the extent $L = b - a$ of the overlap region is much larger than the coherence length l_c . The field amplitude exiting the nonlinear medium is then proportional to the integral

$$\int_0^d g(z) e^{i\Delta kz} dz = \frac{1}{i\Delta k} g(z) e^{i\Delta kz}\Big|_0^d - \frac{1}{i\Delta k}\int_0^d g'(z) e^{i\Delta kz} dz , \tag{2}$$

where partial integration has been used. The properties of the weighing function $g(z)$ imply that its derivative $g'(z)$ is also a smooth function with a maximum value on the order of $|g'(z)| \approx 1/L$. The second term in Eq. (2) can then be approximated as

$$\frac{1}{i\Delta k}\frac{1}{L}\int_0^d e^{i\Delta kz}dz = \frac{1}{i\Delta k}\frac{l_c}{i\pi L}\left[e^{i\Delta kd} - 1\right], \tag{3}$$

which is weaker than the first term in Eq. (2) by a factor on the order of l_c/L. The second term can therefore be neglected unless the first term vanishes.

The first term in Eq. (2) depends on where the beam overlap is localized with respect to the nonlinear material. We first consider the case where the overlap region is large compared to the length of the material (a << 0 and b >> d). The function $g(z)$ can then be taken as constant across the material, and the generated field amplitude becomes proportional to

$$\frac{1}{i\Delta k} g(0)\left(e^{i\Delta kd} - 1\right), \tag{4}$$

which again leads to Maker fringes as in Eq. (1).

We next localize the overlap near a boundary of the nonlinear medium, i.e., we take $a < 0$, $0 < b < d$ (front surface) or $0 < a < d$, $b > d$ (back surface). As $g(d) = 0$ in the first case and $g(0) = 0$ in the second, the generated field amplitudes become proportional to, respectively,

$$-\frac{1}{i\Delta k} g(0) \quad \text{and} \quad \frac{1}{i\Delta k} g(d)e^{i\Delta kd}, \tag{5}$$

Two interesting observations can be made from Eqs. (5). First, the amplitude is proportional to the value of the overlap function at the boundary. In other words, when the overlap is translated across the boundary, the amplitude reproduces the shape of the function $g(z)$. The maximum amplitude is obtained when the beam overlap is centered at the boundary, and corresponds to half of the Maker-fringe maximum of Eq. (4). Second, not only the magnitude, but also the phase of the generated amplitude is determined by the position of the boundary. This corroborates the idea that the signal from the bulk of a well characterized material can be used to determine the phase of the signal from its surface or from a thin film deposited on it [10].

We finally consider the situation where the input beams overlap deep inside the bulk of the nonlinear material ($a > 0$ and $b < d$). In this case, $g(0) = g(d) = 0$ and the first term in Eq. (2) vanishes identically. Since only the second term in the equation survives, the generated field amplitude is suppressed by a factor on the order of l_c/L as compared to the signal obtained when the beams overlap at the boundary.

3. Experimental results and discussion

In our experiments, a Q-switched Nd:YAG laser (1064 nm, up to 20 mJ, 10 ns, 30 Hz) was used as a source for two-beam second-harmonic generation [11]. The laser output was split into two beams of nearly the same intensity. A weak lens (f = 50 cm) was placed before the beam splitter. The spot size of the beams at the sample was approximately 0.5 mm and their confocal range was on the order of 50 cm, which is much larger than the extent of the overlap region and the thickness of any of the samples studied. The input beams were therefore plane-wave-like except for their transverse profiles. Second-harmonic light generated by the sample was detected in the transmitted direction by a photomultiplier tube.

We first investigated a 12 mm thick glass (BK7) plate, whose bulk response is electric-dipole-forbidden and arises from the higher multipole contributions to the second-order nonlinear response [12-15]. The incident angles of the fundamental beams were 35° and 50°. One beam was polarized in the plane of incidence (p-polarized) and the other perpendicular to it (s-polarized), as the bulk contribution is best accessed in this configuration [12-15]. The

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extent of the overlap region and the coherence length were estimated to be, respectively, $L \approx$ 5 mm and $l_c \approx$ 20 μm. The second-harmonic signal was recorded when the glass plate was translated through the overlap of the fundamental beams (Fig. 2). One can clearly observe that the highest signal is obtained when the center of the beam overlap is localized near the front or the back surface of the sample.

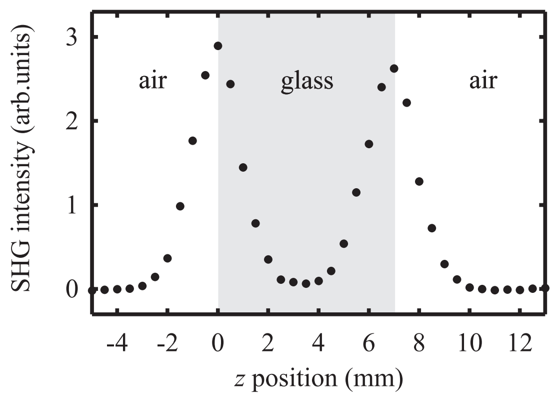

Fig. 2. Second-harmonic (SHG) signal obtained by translating the overlap of the input beams across a 12 mm thick glass plate (BK7). The signal is strongly suppressed when the beams overlap deep in the bulk of the material. The surfaces appear to be closer than the physical thickness of the sample because of refraction.

We realize that the results of Fig. 2 could be interpreted as a proof of surface origin of the nonlinearity. The interpretation is tempting because the bulk response of glass is electric-dipole-forbidden and therefore relatively weak. However, we [12,13] and others [14,15] have recently shown that polarization analysis allows the bulk and surface contributions to be addressed separately. Such measurements reveal that our signal arises almost entirely from the bulk [12,13]. One could also argue that the results are due to different propagation directions of the signals generated deep in the bulk and near the surface. When the nonlinear response is localized in the bulk, the wave vector of the generated field $\mathbf{k}_3$ is expected to be parallel to $\mathbf{k}_1 + \mathbf{k}_2$. When the interaction volume extends across a boundary of the material, however, the generated field propagates along a direction which can slightly deviate from $\mathbf{k}_1 + \mathbf{k}_2$ [16]. Although the change is small (0.3° in our geometry) and within the acceptance angle of the detector, we scanned the detector to make sure that the signal is truly suppressed in the bulk.

To further exclude these alternative explanations and to highlight the universal character of the effect, we repeated the experiment using several nonlinear crystals (quartz, KTP, DKDP) with an electric-dipole-allowed response. Although the interaction had a relatively strong phase mismatch, the overall signal from the crystals was orders of magnitude larger than that from glass, and therefore clearly of bulk origin. Furthermore, the input beams were applied symmetrically on the crystals (incident angles of +10° and -10°) so that the second-harmonic signal always propagates along the surface normal [16]. All measurements confirmed our theoretical predictions. The results obtained, for example, with a 16.4 mm thick DKDP crystal and orthogonally polarized input beams are shown in Fig. 3.

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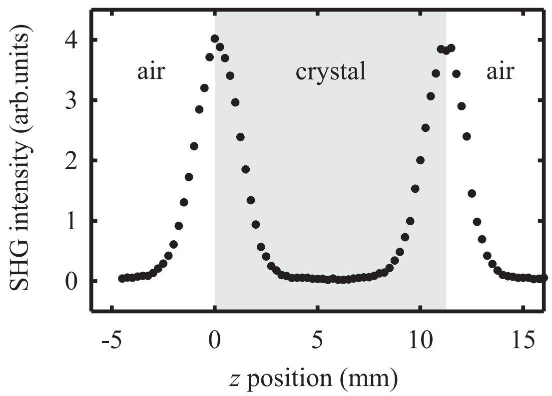

Fig. 3. Second-harmonic (SHG) signal obtained by translating the overlap of the input beams across a 16.4 mm thick nonlinear crystal (DKDP). The strongest signal is obtained near the crystal surfaces, whereas practically no signal is detected from the bulk of the crystal.

To get more physical insight to the results, we consider the contributions of successive polarization sheets to the nonlinear signal (Fig. 4). Perfect phase matching would imply that all contributions are in phase leading to linear growth of the signal amplitude over the interaction length. On the other hand, phase mismatch leads to infinitesimal phase differences between successive polarization sheets. If the contribution from every sheet is of equal strength, the resulting field amplitude describes a circle on the complex plane and returns to the origin after two coherence lengths (Maker fringes). When the interaction is gradually turned on, however, the circle must be replaced by an expanding spiral centered at the origin. The spiral reaches its maximum size at the center of the overlap region (where the amplitude is exactly half of the Maker-fringe maximum) and starts contracting after that. As the beginning phase of the contracting spiral is determined by the final phase of the expanding spiral, the contracting spiral converges back to origin giving rise to no net signal from the whole interaction volume. In other words, the signals from the two halves of the interaction volume interfere destructively producing essentially no net signal.

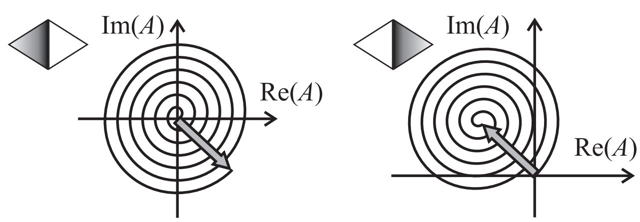

Fig. 4. Nonlinear optical signal arising from a non-phase-matched interaction acting over a finite volume. Phase mismatch leads to infinitesimal phase differences between successive polarization sheets. As the interaction is gradually turned on, the resulting amplitude (A) describes an expanding spiral centered at the origin. The spiral contracts back to the origin when the interaction is gradually turned off. The field amplitudes (arrows) resulting from the two halves of the interaction volume are seen to interfere destructively producing essentially no net signal.

We note that the effect described here has some similarities with harmonic generation by focused beams [1]. It is well known that even a single, tightly focused Gaussian beam cannot give rise to harmonic signals in bulk materials in case of negative phase mismatch (as typically occurs in materials with normal dispersion). The effect is related to the additional

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(Gouy) phase shifts that Gaussian beams experience in passing through the focus and arises only when the confocal range of the beams is much shorter than the length of the nonlinear medium. In contrast, the effect described here also applies for the case of nearly collimated beams and does not depend on the sign of the phase mismatch. We also note that results similar to ours have been recently observed by others with two-beam second-harmonic generation [15].

We believe that our results have broad implications in several subfields of nonlinear optics. It is often difficult to separate the surface and bulk contributions to the nonlinear signals [17-20]. To isolate the bulk contribution, it would make sense to localize the interaction deep in the bulk to avoid any surface contribution. However, the present results show that even the bulk contribution is then suppressed because of phase matching issues. Conversely, when measuring the nonlinear response of a surface or an interface one needs to be especially concerned about the influence of bulk contributions, as these are maximized precisely in such geometry. Therefore, our results emphasize the importance of detailed polarization measurements in establishing the origin of the nonlinear signal [12-15].

As already mentioned, the early results regarding the strength of the electric-dipole-allowed sum-frequency generation in chiral materials [5,6] have recently been challenged [7-9]. Our results show that the measured signals can vary by several orders of magnitude depending on the experimental geometry and on whether the interaction is localized near the surface or deep in the bulk of the material. The various results should therefore be compared with due care and considering the details of the experimental geometry, which are not available from all the published work.

4. Conclusions

We have shown that nonlinear optical signals generated by non-phase-matched interactions are strongly suppressed when the interaction volume is finite and localized deep inside the bulk of a homogeneous material. Even when the nonlinear response has bulk origin, the strongest signals are obtained when the interaction is localized near the surface of the nonlinear medium. The effect is not limited to second-order nonlinear processes but applies to all phase-mismatched processes where the strength of the interaction is turned on and off gradually. This includes, e.g., processes that are driven by noncollinear input beams of finite transverse size or processes occurring in materials whose nonlinearity grows from zero to a maximum value and then decreases back to zero over distances that are much larger than the coherence length. Due to its universal character, the effect has broad implications in nonlinear optics and could explain contradictory results regarding nonlinear optical response of chiral liquids.

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