Fresnel enhancement in second-harmonic generation from rear surfaces of transparent media

P. Tepper, J. C. Zink, J. Reif, and E. Matthias
Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, D-1000 Berlin 33, Federal Republic of Germany
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With the objective of checking for higher-order bulk contributions, we measured *s*-polarized second-harmonic generation (SHG) in reflection from front and rear surfaces of transparent centrosymmetric crystals. We find an enhancement by up to almost an order of magnitude of the SHG yield from the rear surface compared with the one from the front surface. The dependence of SHG yield on angle of incidence is in excellent agreement with theoretical predictions based on pure dipole interaction at each surface. This result assures surface specificity for SHG in reflection on transparent crystals.

Optical second-harmonic generation (SHG) in reflection from centrosymmetric crystals has become a well-established tool for the investigation of electronic and geometrical properties of surfaces exposed to different ambients,[1-7] of adsorbates,[8-10] and of interfaces.[11] In general, however, it is difficult to distinguish between surface-specific contributions and higher-order contributions[12,13] from the bulk to the SHG yield. This problem is inherent when studying substances in which one of the two wavelengths involved is absorbed,[14,15] even if both the fundamental and second harmonic radiation are *s* polarized,[16] a situation for which most of the higher-order contributions vanish.[12] On the other hand, for materials which are transparent to both fundamental and second-harmonic radiation, there is evidence[17,18] that under certain experimental conditions bulk contributions can be ruled out. It is the purpose of this Brief Report to present experimental proof for this conjecture. It implies that surfaces of centrosymmetric wide-band-gap crystals can indeed be studied by SHG techniques without any ambiguity.

The great disadvantage encountered when applying the SHG technique to transparent materials is the extremely weak second-harmonic yield.[19] However, this can be considerably improved by utilizing the fact that the electric field at the exit surface of a crystal is larger than at the entrance, since there is no phase shift upon reflection. Evidence for this comes, for example, from observations of laser-induced damage on entrance and exit faces of optical components.[20] In this Brief Report we show that the higher electric field of the fundamental light at the exit surface also leads to a significant enhancement of the SHG yield reflected from that surface. Experimentally, this was realized by measuring the dependence of *s*-polarized SHG on the angle of incidence of *s*-polarized fundamental light for both the entrance and exit surface of a polished BaF_2 (111) single crystal (Fig. 1). The experimental results can be well described by the second-order Fresnel coefficients appropriate for SHG in reflection.[21]

Experimentally, the second harmonic was generated by 6-ns pulses of a frequency-doubled (532-nm) Nd-doped yttrium aluminum garnet laser, with typical intensities around 2 MW/cm^2, in reflection from polished BaF_2 (111) surfaces in air (see Ref. 17 for more details). The thickness of the crystal was such that the second-harmonic signal from the entrance surface could be spatially well separated from the one originating at the exit surface. The azimuthal crystal orientation was optimized to give the maximum SHG yield for *s* polarization,[17] i.e., the electric field is oscillating along the $\langle \bar{1}\bar{1}2 \rangle$ direction. The angle of incidence at the front side (see Fig. 1) could be varied between $15° \leq \theta \leq 75°$. The *s* polarization of both fundamental and second-harmonic light was most carefully controlled by means of Glan prisms with an extinction ratio larger than 10^5. The reliability of the experimental setup was tested by measuring the reflection of the fundamental beam and comparing it with the expected linear Fresnel dependence. This comparison is displayed in Fig. 2. The experimental results (indicated by stars) of the SHG as a function of angle of incidence are shown in Fig. 3, together with the theoretical predic-

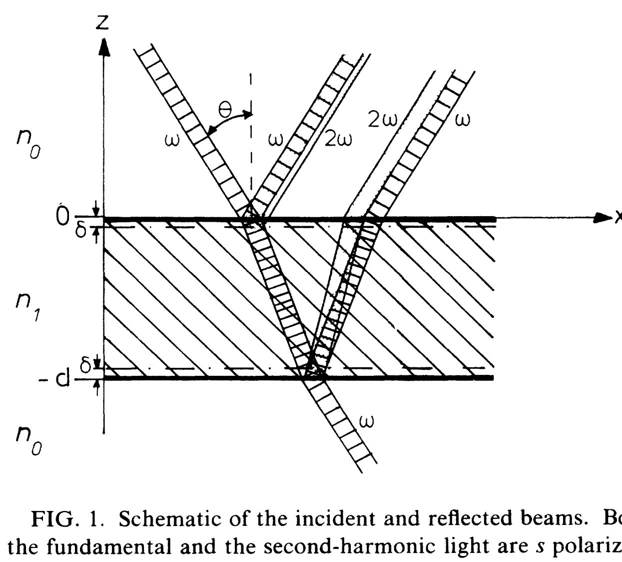

FIG. 1. Schematic of the incident and reflected beams. Both the fundamental and the second-harmonic light are *s* polarized. The crystal has the index of refraction n_1, the ambient air n_0. The angle of incidence θ is measured on the low-index side.

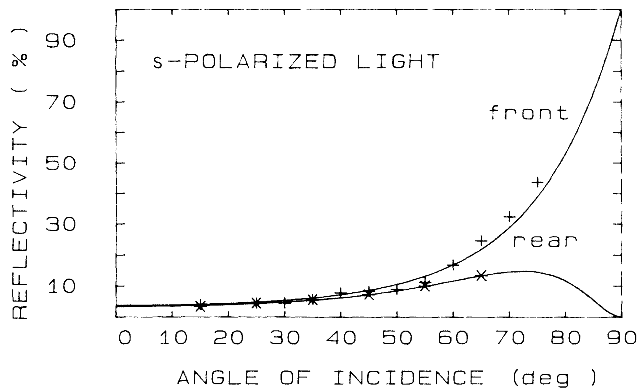

FIG. 2. Linear reflectance of the s-polarized fundamental light (532 nm) for the entrance and exit surface of BaF_2. A comparison between the Fresnel predictions (solid lines) and the experimental data (error $\pm 10\%$; crosses for entrance face, stars for exit face) served to test the experimental setup.

tions (solid lines) outlined below. It should be noted that only the absolute value of the susceptibility tensor element χ_{111} had to be adjusted in order to obtain the excellent agreement between theory and experiment.

The theoretical prediction is based on the assumption that, for centrosymmetric transparent crystals and s-s-polarized radiation, dipole interaction at the surface is exclusively responsible for the SHG in reflection. Under this premise, we will derive the nonlinear Fresnel coefficients[21] for SHG at both surfaces. If these are sufficient to completely describe the experimental data, we will consider this as proof that bulk contributions are negligible.

The nonlinear polarization induced by pure dipole interaction[22] is given by the relation

$$\mathbf{P}(2\omega)=\boldsymbol{\chi}^{(2)}:\mathbf{E}(\omega)\mathbf{E}(\omega) , \tag{1}$$

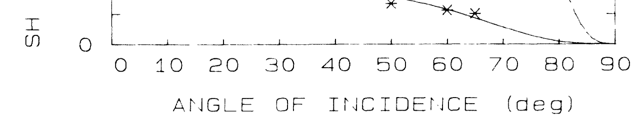

FIG. 3. Dependence of second-harmonic yield at the entrance and exit surfaces on angle of incidence for s-s polarization. Solid lines represent theoretical predictions based on surface dipole interaction only, stars mark the experimental data. S-input represents s-polarized input; s-SH represents s-polarized SHG.

where $\boldsymbol{\chi}^{(2)}$ is the second-order susceptibility tensor. We assume this polarization to exist only in sheets of thickness δ, with $\delta/\lambda \ll 1$, at the two surfaces where the bulk symmetry is broken[23-25] (cf. Fig. 1). An s-polarized plane wave of frequency ω, incident from the optically thin region $(z>0)$ under angle θ, sets up the effective driving fields for the nonlinear polarization. In previous experiments on laser-induced surface damage,[20] Boling, Crisp, and Dubé demonstrated that macroscopic Fresnel equations can be applied to obtain the ratio of laser intensities between front and exit surface layers of a transparent dielectric slab. Consequently, we obtain at the entrance side $(0>z>\delta)$

$$\mathbf{E}_0(\omega)=E_{\rm in}t_{01}\mathbf{s}\exp(ik_x x) , \tag{2}$$

and at the exit side $[-(d-\delta)>z>-d]$

$$\mathbf{E}_d(\omega)=E_{\rm in}t_{01}(1+r_{10})\mathbf{s}\exp[i(k_x x-k_z d)] . \tag{3}$$

The subscript 0 or 1 indicates the low- or high-index region, respectively. Hence t_{01} denotes the linear Fresnel coefficient for s-polarized transmission from low- to high-index medium and r_{10} the one for reflection at the opposite (exit) boundary. For simplicity we assume the low-index medium to be a vacuum. The vector $\mathbf{s}$ denotes the polarization which according to Fig. 1 is along the $\mathbf{y}$ direction. From Eq. (3) it follows that at the exit face the field $\mathbf{E}_d(\omega)$ of the fundamental wave is larger by a factor of $(1+r_{10})$ compared to the field at the entrance face. When inserting it into Eq. (1), this gives rise to the expected enhancement of the second-harmonic polarization at the exit surface.

For a more detailed analysis we can, following notation introduced by Sipe and Mizrahi,[24-26] combine the respective Fresnel coefficients and the polarization vector to a generalized polarization vector $\mathbf{e}$. This leads to a factorization which shows explicitly the dependence of the SHG on the angle of incidence, and one obtains for the second-harmonic power[24-27]

$$\mathcal{P}(2\omega)=C\sec^2\theta|\mathbf{e}^*\boldsymbol{\chi}^{(2)}:\mathbf{ee}|^2\mathcal{P}^2(\omega) . \tag{4}$$

Here $\mathbf{e}^*$ is the generalized polarization vector of the second harmonic and $C=32\pi^3\omega^2/(c^3A)$, where A is the area of the incident beam normal to the Poynting vector and c is the speed of light. Now one can combine the linear Fresnel factors, contained in the generalized polarization vectors, to yield second-order Fresnel factors, expressed in terms of the vector components[28]

$$F_{ij}=e_i^*e_k e_l\sec\theta . \tag{5}$$

These components contain all geometrical information about the light, such as angle of incidence, polarization of the fundamental, and polarization of the second harmonic. Using Eq. (5), the second-harmonic power can be expressed in the following way:

$$\mathcal{P}(2\omega)=C\left|\sum_{i=1}^{3}\sum_{j=1}^{6}F_{ij}S_{ij}\right|^2\mathcal{P}^2(\omega) . \tag{6}$$

The tensor $\mathbf{S}$ is the projection of the second-order susceptibility $\boldsymbol{\chi}^{(2)}$ onto laboratory coordinates, and its components S_{ij} describe all geometrical variations of the crystal, as for example the azimuthal dependence of the susceptibility. By means of Eqs. (5) and (6), the second-harmonic power generated at the two BaF_2 (111) surfaces can be calculated as a function of the angle of incidence. Making use of the appropriate C_{3v} symmetry of the second-order susceptibility, Eq. (6) is explicitly given by

$$\mathcal{P}(2\omega)=C|(1+R_{01})t_{01}^2\sec\theta\chi_{111}\sin(3\psi)|^2\mathcal{P}^2(\omega) \quad (7a)$$

for the front surface, and

$$\mathcal{P}(2\omega)=C|T_{01}T_{10}[t_{01}(1+r_{10})]^2\sec\theta\chi_{111} \times\sin(3\psi)|^2\mathcal{P}^2(\omega) \quad (7b)$$

for the rear surface (capital letter Fresnel coefficients are taken at 2ω, ψ is the angle between **s** and the crystallographic $\langle\bar{1}\bar{1}2\rangle$ direction). The result is shown by the solid lines in Fig. 3. Notice that at $\theta=63°$ a close to ninefold enhancement of the signal from the exit face over the one from the entrance face is predicted and confirmed by the experimental data.

The conspicuous agreement between theory and experiment justifies the choice of dipole interaction at the surface as the *only* source of the observed second-harmonic yield [cf. Eq. (1)]. It confirms the postulate of Ref. 17, that for a material transparent to both wavelengths there is no "anisotropic," i.e., *s*-*s*-polarized, bulk contribution, in contrast to observations in absorbing materials.[14-16] To further support this conclusion, we calculated for both surfaces the dependence of such quadrupolar bulk contribution on angle of incidence along the lines of Mizrahi and Sipe.[24] The results are in complete disagreement with the experimental data,[29] as is shown in Fig. 4. In particular, the limited coherence length inside the bulk would lead to a yield modulation as a function of incident angle,[30] and there is no reason to expect such additional contributions for the exit face in view of the good agreement of the data with the dipolar predictions in Fig. 3.

The discrepancy between the results from transparent and absorbing materials may be understood as follows. When second-harmonic generation is viewed as a three-photon transition, for higher-order contributions either the second harmonic or one of the fundamental photons must be associated with the electric quadrupole or magnetic dipole interaction. In an absorbing medium, it may be distinguished, whether the resonant transition is of electric dipole or of higher-order character. In a transparent system, however, the two possible interaction schemes are indistinguishable. This results in a destructive interference[31,32] of the "anisotropic" contributions [cf. Eq. (6) of Ref. 17].

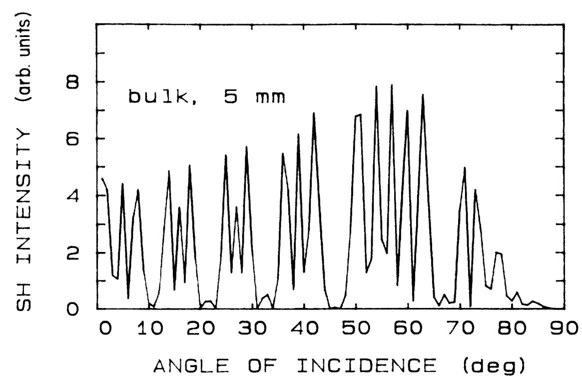

FIG. 4. Expected dependence of bulk second-harmonic yield on angle of incidence (reflected at the exit surface).

In summary, we have demonstrated that, by proper choice of polarization, SHG at surfaces of transparent centrosymmetric media is free of higher-order bulk contributions. This was proved by comparing the second-harmonic yields of the entrance and exit surfaces with theoretical predictions based on surface dipole interaction only. The signal from the exit surface was found to be substantially larger than that from the front surface, which can be beneficially exploited in this low signal technique. Experiments on this effect for *p*-polarized light, where the situation becomes more complicated because of the additional higher-order terms, will be the subject of a forthcoming publication.[29]

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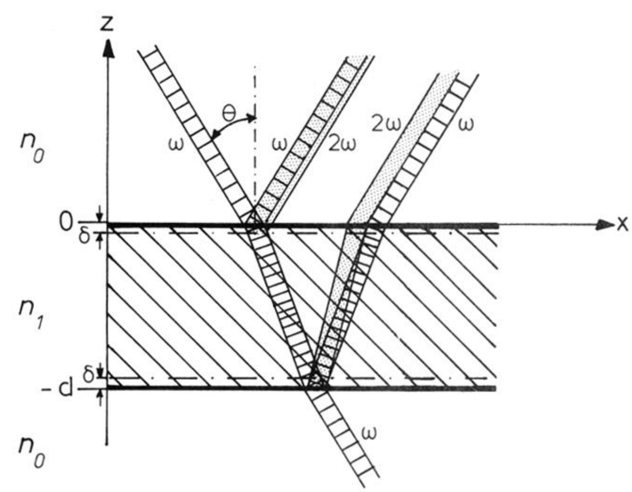

FIG. 1. Schematic of the incident and reflected beams. Both the fundamental and the second-harmonic light are s polarized. The crystal has the index of refraction n_1, the ambient air n_0. The angle of incidence θ is measured on the low-index side.