Calibration of the second-order nonlinear optical susceptibility of surface and bulk of glass

Francisco J. Rodriguez*, Fu Xiang Wang, and Martti Kauranen

Department of Physics,Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland
Corresponding author: francisco.rodriguezmartinez@tut.fi

Abstract: A two-beam second-harmonic generation technique is developed to calibrate the magnitude of the second-order nonlinear optical susceptibility components of surface and bulk (multipolar origin) of isotropic materials. The values obtained for fused silica calibrated against χ_{XXX} of crystalline quartz are $\chi_{\parallel\parallel\perp} = 7.9(4)$, $\chi_{\perp\parallel\parallel}+\gamma = 3.8(4)$, $\chi_{\perp\perp\perp}+\gamma = 59(4)$, and $\delta' = 7.8(4)$ in units of 10^{-22} m^2/V. Similar values are obtained for BK7 glass. An alternative way of calibration against χ_{XYZ} of quartz is demonstrated. The technique could also be extended to characterize the susceptibility tensor of crystals as a convenient alternative to the Maker-fringe technique.

OCIS codes: (190.2620) Harmonic generation and mixing; (190.4350) Nonlinear optics at surfaces; (160.2750) Glass and other amorphous materials

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Second-order nonlinear optical effects are useful tools for surface, thin film and interface studies because of their inherent surface specificity and the possibility to access buried interfaces [1, 2]. This is because, within the electric-dipole approximation of the light-matter interaction, second-order effects are forbidden in the bulk of centrosymmetric materials but allowed at surfaces, where the centrosymmetry is broken. However, second-order effects become allowed in centrosymmetric bulk materials due to higher multipole (magnetic-dipole and electric-quadrupole) effects [1, 3]. Due to the longer interaction zone in the bulk, the multipolar contributions can lead to nonlinear signals that are comparable to those from the surface contributions. Moreover, part of the multipolar bulk contribution cannot be distinguished from the surface effects [4]. It is therefore important for thin film and surface studies based on second-order techniques to know the magnitudes of all the measurable optical parameters of the substrate. Very few studies exist regarding the calibration of surface nonlinearities and even fewer regarding the multipolar bulk contributions [5, 6].

In a previous paper [7], we reported the determination of the relative values of the tensor components of the effective dipolar surface nonlinearity and the separable multipolar bulk nonlinearity of BK7 glass. In this paper, we develop a method to calibrate their absolute values against a well known reference material. Our method is based on two-beam second-harmonic generation (SHG), which is needed to access the multipolar bulk contributions, but also offers a simplified way for calibration compared to the traditional techniques. We present the calibrated results for BK7 glass and fused silica (amorphous SiO_2) samples using quartz (crystalline SiO_2) as reference. Both glasses are used as common substrates for thin films.

Traditionally, the calibration of the second-harmonic (SH) nonlinear susceptibility has been based on the Maker-fringe method [8]. In this method, the thickness of the nonlinear material traversed by light is varied by tilting the sample or by translating a wedge-shaped sample. This variation produces a pattern of interference maxima and minima in the intensity of SHG, which originate from the difference in the phase velocities of the fundamental and SH wavelengths. Yet, this method can lead to large uncertainties in the calibrated values because of multiple reflections between the surfaces of the samples [9, 10]. One method that avoids the fringe analysis makes use of samples with a large wedge to separate the free and driven SH waves [11, 12]. However, in both cases, the use of only one fundamental beam makes the technique insensitive to some of the multipolar bulk contributions as explained below. The two-beam method used in the present work allows a simple calibration of the bulk signals provided that the sample thickness is sufficient and also eliminates the need for fringe analysis. In the present paper, we use the new method to calibrate the surface and multipolar bulk SHG of isotropic glass samples. However, it is clear that the technique could also be adapted to characterize dipole-allowed bulk SHG responses of noncentrosymmetric crystals and multipolar bulk SHG of centrosymmetric crystals. The use of two fundamental beams whose polarizations can be controlled independently could be convenient in the tensorial characterization of crystals with low symmetry.

Two-beam SHG has the property that, even though it has bulk origin, the signal vanishes when the overlap of the two beams is completely located inside the bulk (see Fig. 1). On the contrary, the signal has a maximum when the overlap is centered at one of the surfaces. This surprising behavior has its origin in phase-matching issues [13]. Thus, for a sample with thickness much less than the overlap length, Maker-fringe modulation of the SH intensity would occur as the sample thickness is varied. On the contrary, when the sample thickness extends beyond the end of the overlap, no modulation occurs. In our experiments, we measure the value of the SHG from glass and quartz when the overlap is centered at the first surface of thick samples: the first half of the overlap is then located in air while the second half is inside

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the material. The intensity of the SH signal in this situation can be shown to correspond to half of the intensity maximum in a Maker-fringe experiment [13].

The SH response of achiral isotropic surfaces like those of glass ($C_{\infty v}$ symmetry) is described by a susceptibility tensor with three independent components: $\chi_{\perp\parallel\parallel}$, $\chi_{\parallel\parallel\perp}$ and $\chi_{\perp\perp\perp}$ where $\perp$ denotes the surface normal and $\parallel$ denotes any direction parallel to the surface [3]. This tensor includes both dipolar and multipolar contributions arising from the structural discontinuity that breaks the centrosymmetry and from the strong gradients in the fields and the material at the surface, respectively [3, 14, 15]. On the other hand, the multipolar response of the isotropic bulk is described by three parameters [1, 4]: β, γ, and δ', which can be expressed as combinations of electric-quadrupole and magnetic-dipole tensors [16]. The SH polarization of the bulk is then $\mathbf{P}^{bulk}(\mathbf{r}) = \beta\,\mathbf{e}(\mathbf{r})\left[\nabla\cdot\mathbf{e}(\mathbf{r})\right] + \gamma\,\nabla\left[\mathbf{e}(\mathbf{r})\cdot\mathbf{e}(\mathbf{r})\right] + \delta'\left[\mathbf{e}(\mathbf{r})\cdot\nabla\right]\mathbf{e}(\mathbf{r})$, where $\mathbf{e}(\mathbf{r})$ is the fundamental field. The first term vanishes for homogeneous media and the second term behaves like the surface contribution so that the measurable quantities are the combinations $\chi_{\perp\perp\perp}+\gamma$ and $\chi_{\perp\parallel\parallel}+\gamma$. Thus, the only bulk parameter that can be separated form the surface is δ'. The term with δ' vanishes when the fundamental field is a single plane wave. However, it can be determined by detecting the SH signal generated jointly by two non-collinear beams at the fundamental frequency.

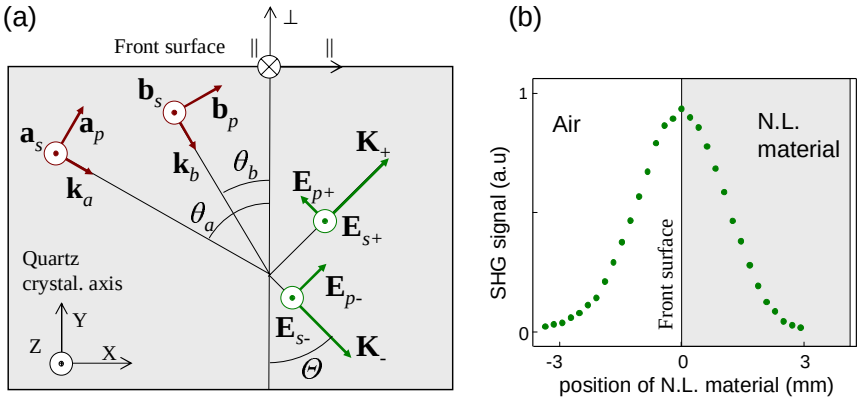

Fig. 1. (a). Geometry of the fundamental (lower-case letters) and SH (upper-case letters) fields inside the nonlinear material (glass or quartz) and orientation of the crystallographic axes for the case of quartz. (b). SH intensity as a function of the relative position of the overlap of the two fundamental beams and the surface of the nonlinear material. The maximum of the peak corresponds to the overlap centered at one of the surfaces.

In the following, we will give expressions for the SH signals from glass and crystalline quartz in an experiment where the overlap of the two fundamental beams is centered at the first surface of the sample and the sample extends beyond the end of the overlap. To do this, we consider the geometry of Fig. 1.

The *s* and *p* components of the SHG field from the glass (surface and multipolar bulk contributions) are given in transmission (lower signs) and in reflection (upper signs) by [7]

$$E_{s\pm} = i\frac{8\pi\omega}{Nc\cos\Theta}\left(\left(\chi_{\parallel\parallel\perp}\sin\theta_a + \delta'\frac{\omega n}{2c\Delta k_{\pm}}\sin(\theta_a-\theta_b)\right)a_p b_s + \left(\chi_{\parallel\parallel\perp}\sin\theta_b - \delta'\frac{\omega n}{2c\Delta k_{\pm}}\sin(\theta_a-\theta_b)\right)a_s b_p\right)$$

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$$E_{p\pm} = i\frac{8\pi\omega}{Nc}((\mp\chi_{\parallel\parallel\perp}\sin(\theta_a+\theta_b)+(\chi_{\perp\parallel\parallel}\cos\theta_a\cos\theta_b+\chi_{\perp\perp\perp}\sin\theta_a\sin\theta_b)\tan\Theta \\ +\delta'\frac{n}{4N\cos\Theta}\sin(\theta_a-\theta_b)(\cos\theta_a-\cos\theta_b))a_p b_p+\chi_{\perp\parallel\parallel}\tan\Theta a_s b_s) \quad (1)$$

where a and b are the amplitudes of the two fundamental beams (with frequency ω), $\Delta k_{\pm} = (n(\cos\theta_a+\cos\theta_b)\pm N\cos\Theta)2\omega/c$ are phase mismatches and n and N the refractive indices of glass at the fundamental and SH frequencies, respectively. The propagation angle Θ of the SH beams is given by the momentum conservation along the surface: $N\sin\Theta = n(\sin\theta_a+\sin\theta_b)/2$. In all these expressions, the fields and angles are considered inside the material. To relate the external and internal quantities in a real experiment, it is necessary to use Snell's law and the appropriate Fresnel coefficients. In our calculations of the SHG detected in transmission we also included the SHG that is generated backwards and then reflected by the front surface of the sample.

The SHG from crystalline quartz arises mainly from the dipolar bulk contribution. The quartz crystal has D_3 symmetry and its second-order susceptibility has four independent components: $\chi_{XXX} = -\chi_{XYY} = -\chi_{YYX} = -\chi_{YXY}$, $\chi_{XYZ} = -\chi_{YXZ}$, $\chi_{XZY} = -\chi_{YZX}$ and $\chi_{ZXY} = -\chi_{ZYX}$. In the case of SHG, the second and third are the same and the fourth is zero. The nonzero values are $\chi_{XXX} = 0.80$ pm/V and $\chi_{XYZ} = 0.017$ pm/V [17].

To find the general functional form of the SH signals from quartz, we first assume that its birefringence is negligible. In that case, the SH field from Y-cut quartz oriented with the Z axis in the *s* direction (Fig. 1) is given by the expression

$$E_{s\pm} = 0$$
$$E_{p\pm} = \frac{8\pi\omega}{N_o c\cos\Theta\Delta k_{\pm}}(\chi_{XXX}(\cos(\theta_a+\theta_b\mp\Theta)a_p b_p \\ +\chi_{XYZ}(\sin(\theta_a\pm\Theta)a_p b_s+\sin(\theta_b\pm\Theta)a_s b_p)) \quad (2)$$

The index of refraction for the SH light (always *p* polarized) is the ordinary index of quartz N_o(532 nm) = 1.5469. However, the index for the fundamental wavelength depends on the polarization. For *p* polarization it will be the ordinary index n_o(1064 nm) = 1.5341 while for *s* polarization it will be the extraordinary index n_e(1064 nm) = 1.5428. Thus, it is necessary to consider different values of $\Delta k_{\pm}$ and of the angles inside the material in Eq. (2) and also different values of the Fresnel coefficients depending on the fundamental beam polarizations.

Note that the SH signals from two-beam SHG can always be expressed in the generic form $E_i = f_{ijk}\, a_j\, b_k$, where *i*, *j* and *k* are *s* or *p* and we assume summation over repeated indices. The coefficients f_{ijk} for glass and quartz can be obtained from Eqs. (1) and (2), respectively. To calibrate the glass parameters against χ_{XXX} of quartz we choose *p*-polarized fundamental beams and detect *p*-polarized SHG. In this way, we are able to measure the signals from both glass and quartz without the need to change the polarizations. It also makes the analysis simpler because only the ordinary refractive index of quartz is used. If the intensity of the fundamental beams is kept constant, the ratio of the SHG intensity between the glass sample and the quartz reference when all the fields are *p* polarized is $I_{SHG}^{glass}/I_{SHG}^{quartz} = \left|f_{ppp}^{glass}\right|^2/\left|f_{ppp}^{quartz}\right|^2$. The ratio of SHG intensity is measured experimentally by changing the glass sample to the quartz reference and using neutral density filters to keep the photomultiplier tube used for the detection in the range of linear response. The value of f_{ppp}^{quartz} is calculated from Eq. (2) and the tabulated susceptibility of quartz. With all this we obtain a calibrated value of f_{ppp}^{glass}.

The values of the tensor components of glass are then calculated by performing a polarization analysis of the glass sample [7]. We keep the polarization of one of the

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fundamental beams always linear while we modulate the polarization of the other beam, initially *p*, with a rotating quarter-wave plate. The SHG generated by the two beams is detected after passing through a polarizer oriented at different angles. We use four measurements of SHG vs. quarter-wave plate angle for various combinations of polarizations (*s*, *p* or 45°) of the linearly polarized fundamental beam and the SH beam. The fitting of three such measurements already yields the relative values of f_{ppp}^{glass}, f_{pss}^{glass}, f_{ssp}^{glass} and f_{sps}^{glass}. The fourth measurement can be used as a check of the experimental setup or to find the best simultaneous fit of the four measurements for more accurate values. From the calibrated values of all the f_{ijk}^{glass} we obtain the susceptibility tensor components using Eq. (1).

In the experiments we used a diode-pumped, Q-switched Nd:YAG laser (1064 nm, 40 mJ, 8 ns, 100 Hz). For the fused silica sample, we used incident angles θ_a = 30° (linearly polarized beam) and θ_b = 61° (quarter-wave plate beam). By fitting the four polarization measurements simultaneously with the theoretical expressions (Fig. 2) we obtained the relative values of all the f_{ijk}^{glass} and their absolute values from the calibrated f_{ppp}^{glass}. The tensor components derived from them are shown in Table I.

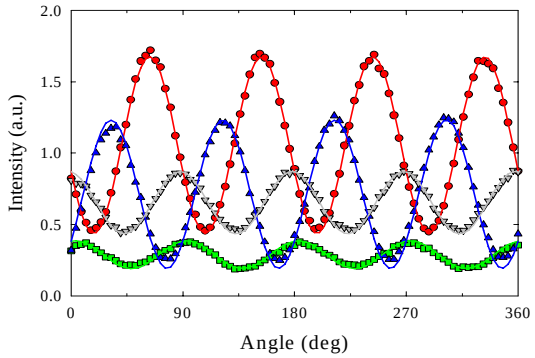

Fig. 2. Measured intensity of SHG from fused silica as a function of the angle of the quarter-wave plate in one fundamental beam for the combinations of the polarization of the other fundamental beam / detected SHG: (circles) 45°/90°, (squares) 45°/0°, (up triangles) 0°/45°, and (down triangles) 90°/45°. The solid lines correspond to fits with the theoretical model.

A second, alternative scheme allows calibrating directly the δ' parameter of glass against χ_{XYZ} of quartz. To make the measurement in glass depend uniquely on the bulk δ' parameter, we set one beam (*a*) to have *p* polarization and to be at normal incidence with respect to the surface (θ_a = 0) and the other beam (*b*) to have *s* polarization. Eq. (1) then becomes

$$E_{s\pm} = i\frac{8\pi\omega^2 n}{Nc^2\cos\Theta\Delta k_{\pm}}\delta'\sin\theta_b a_p b_s, \quad E_{p\pm} = 0. \tag{3}$$

On the other hand, the SHG signal from quartz with the Z axis in the *s* direction is only sensitive to χ_{XYZ} and is given, for both X- and Y-cut quartz by the expression

$$E_{s\pm} = 0, \quad E_{p\pm} = \pm\frac{8\pi\omega}{N_o c\Delta k_{\pm}}\chi_{XYZ}\tan\Theta a_p b_s. \tag{4}$$

Now it is necessary to use the extraordinary refractive index of quartz at the fundamental wavelength to calculate the angle and transmission coefficient of beam *b*. The expression for the phase mismatch is also slightly affected: $\Delta k_{\pm} = (n_o\cos\theta_a + n_e\cos\theta_b \pm N_o\cos\Theta)2\omega/c$ as is also the angle of the SHG beam $N_o\sin\Theta = (n_o\sin\theta_a + n_e\sin\theta_b)/2$. The measurement in

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quartz is very sensitive to the alignment of the (*s*) polarization of beam *b* and the Z axis of quartz. Any small angle between the two directions will introduce a contribution from the much larger χ_{XXX} component of quartz and result in a higher SHG signal.

Using an angle θ_b = -31° and X-cut quartz as the reference we obtained the δ' value shown in Table I for fused silica and BK7 glass. We calculated the rest of the tensor components using the relative values obtained in the polarization analysis described above for the fused silica and the one made previously [7] for BK7. The polarization of beam *b* and the quartz crystal were aligned with a precision better than 15' by minimizing the SH signal to avoid any contribution from χ_{XXX}. However, we still detected about 30% of the SH intensity having *s* polarization while it should have been zero as seen from Eq. (4). This is presently a drawback of this method and can lead to errors in the experimentally determined values. The origin of the problem is unclear, but it may be associated with small polarization rotation in this geometry because of the optical activity of quartz or with a multipolar response of quartz.

Table I. SHG susceptibility tensor components for fused silica and BK7 glass in units of 10^{-22} m^2/V

	Fused silica		BK7
n (1064 nm)	1.4497		1.507
N (532 nm)	1.4608		1.519
	Cal. with χ_{XXX}	Cal. with χ_{XYZ}	Cal. with χ_{XYZ}
$\chi_{\parallel\parallel\perp}$	7.9 ± 0.4	12.1 ± 0.7	14.6 ± 0.8
$\chi_{\perp\parallel\parallel}+\gamma$	3.8 ± 0.4	5.8 ± 0.6	7 ± 2
$\chi_{\perp\perp\perp}+\gamma$	59 ± 4	90 ± 5	93 ± 14
δ'	7.8 ± 0.4	12.0 ± 0.7	14.7 ± 0.8

The error limits in Table I were calculated from the uncertainties in data fitting and conservative uncertainties of 1° in the incident angles and 5% in the transmittance of the neutral density filters. The difference between the two methods, clearly larger than the error limits, could be related to the above drawback of χ_{XYZ} calibration. However, recent work [18] suggests that the relative values of χ_{XXX} and χ_{XYZ} in literature [17] could also be imprecise.

Note that the absolute and relative values obtained for the two types of glass are very similar. This suggests that the second-harmonic response has the same origin in both glasses (see discussion in Ref. [7]) and is little affected by the additives present in BK7.

Compared to the values reported for crystalline silicon surfaces [5], our results for the fused silica surface are 2 orders of magnitude smaller for $\chi_{\perp\parallel\parallel}+\gamma$ and 3 orders smaller for $\chi_{\parallel\parallel\perp}$ and $\chi_{\perp\perp\perp}+\gamma$. The value of the bulk parameter ζ that appears in cubic crystals is also 3 orders of magnitude larger than the δ' of fused silica. The large difference in the magnitudes can be understood by the resonant conditions used in the crystalline silicon measurements and the non-resonant conditions in our fused silica measurements. In addition, Wei, *et al.*,[6] have measured the sum-frequency-generation surface susceptibility of an octadecyltrichlorosilane monolayer on a fused silica substrate obtaining nonresonant values of the substrate effective susceptibility on the order of 10^{-22} m^2/V, very close to the ones reported.

To summarize, we have developed a technique based on two-beam SHG for the calibration of the second-order response of bulk materials including multipolar contributions. We used it to determine the surface and bulk SH susceptibility components of two transparent glasses. The method allows calibrating the susceptibilities of any centrosymmetric material against

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quartz. It could also be extended to calibrate bulk dipolar responses or measure in reflection in absorbing materials.

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