

Giant Enhancement of Surface Second Harmonic Generation in BaTiO₃ due to Photorefractive Surface Wave Excitation

Igor I. Smolyaninov, Chi H. Lee, and Christopher C. Davis

Electrical Engineering Department, University of Maryland, College Park, Maryland 20742

(Received 29 March 1999)

We report observation of strongly enhanced surface second harmonic generation (SHG) in BaTiO₃ due to excitation of a photorefractive surface electromagnetic wave. Surface SH intensity may reach 10^{-2} of the incident fundamental light intensity. Angular, crystal orientation, and polarization dependencies of this SHG are presented. Possible applications of this effect in nonlinear surface spectroscopy are discussed.

PACS numbers: 78.20.Jq, 42.65.Ky, 42.65.Tg, 42.70.Nq

Linear surface electromagnetic waves (SEW) such as surface plasmons or surface polaritons [1] play a very important role in such surface optical phenomena as surface enhanced Raman scattering, surface second harmonic generation (SHG), etc. They are extremely useful in applications such as chemical and biological sensing since the electromagnetic field of a SEW is strongly enhanced near the interface. A linear SEW may be excited at the interface between media with opposite signs for their dielectric constants ϵ , such as at a metal-vacuum interface. Another example is the interface between a vacuum and a dielectric that has a sharp absorption line. Such a dielectric has $\epsilon(\omega) < 0$ for frequencies just above the absorption line. In both cases the SEW free propagation length in the visible range does not exceed a few micrometers because of high losses [1]. This limits the potential advantages of using SEW in surface enhanced nonlinear optical studies and sensor applications.

Recently, a new kind of nonlinear SEW called a photorefractive surface wave has been predicted [2] and observed experimentally [3] in BaTiO₃. This phenomenon is closely related to self-trapped optical beams (also known as spatial solitons) and self-bending beams observed in photorefractive crystals [4]. A photorefractive SEW occurs when a beam self-bent towards the positive direction of the optical axis (the poling direction) undergoes a cycle of deflections towards the face of the crystal and total internal reflections. The resulting nonlinear SEW is localized near the crystal-air interface with a penetration depth as small as $10 \mu\text{m}$ into the photorefractive crystal [2]. This leads to a strong enhancement of the optical field near the interface that is common for all SEWs. On the other hand, since BaTiO₃ is transparent in the visible range, the free propagation length of the photorefractive SEW along the surface is limited only by the size of the crystal. As a result, a very strong enhancement of all nonlinear surface optical phenomena (such as surface adsorbed molecular luminescence, Raman scattering, surface SHG, etc.) may be expected due to photorefractive SEW excitation. This effect may also be used in combination with further field enhancements produced by surface topo-

graphical defects or by the probe tip of a scanning probe microscope [5].

In this Letter we report the first observation of strongly enhanced surface SHG due to the photorefractive SEW excitation in BaTiO₃. Surface SHG in BaTiO₃ is a very suitable phenomenon for demonstrating the potential of photorefractive SEWs in nonlinear surface optics. Phase-matched optical SHG (collinear or noncollinear) is forbidden in the bulk of BaTiO₃ in the visible range because of strong dispersion: The refractive indices for ordinary and extraordinary waves are 2.67 and 2.57, respectively, at 400 nm, and 2.36 and 2.32, respectively, at 800 nm light wavelength [6]. The momentum conservation law cannot be satisfied in the volume SHG process. Thus, in contrast to experiments done with KTP crystals [7], observation of the fundamental and phase-matched SHG fields mutually trapped in the volume spatial solitary wave is impossible in BaTiO₃. On the other hand, phase-matching conditions are modified for the surface SHG. Only the momentum component parallel to the interface must be conserved. This leads to an extremely strong phase-matched surface SHG when a photorefractive SEW is excited.

The surface nature of this SHG, in combination with the strong photorefractivity of BaTiO₃, leads to quite peculiar angular and orientational behavior of the SH light intensity. We believe that our observations performed in a well controlled geometry may clarify a lot of questions concerning still unclear "anomalous" SHG in BaTiO₃ reported recently by a number of groups [8,9]. This is especially important for the rapidly developing field of ferroelectric oxide film growth and characterization. Much recent effort in this field is caused by the applications of these films in nonvolatile ferroelectric random-access memory and dynamic random-access memory devices [10]. SHG has been used to determine the crystallographic orientation and the degree of poling of these films (in particular, BaTiO₃ films in [9]).

Our experimental geometry is shown in Fig. 1. The iron doped crystal of BaTiO₃ from Sanders Inc. used in the experiments is a $8 \text{ mm} \times 8 \text{ mm} \times 8 \text{ mm}$ cube which

was cut with two opposing faces perpendicular to the c axis and poled along the c axis. The crystal was mounted on a three-axis translational and rotational stage. Linearly polarized light from a Ti:sapphire laser operating at a wavelength of 810 nm (repetition rate 76 MHz, 100 fs pulse duration, 30 mW average power) was focused onto the top edge of the crystal. The direction of the beam was parallel to the top face of the crystal.

As the vertical position of the crystal was scanned, very bright second harmonic light emission coming from the top face of the crystal was observed. The brightness of SH emission was very sensitive to the vertical position of the crystal as is evident from Fig. 2(a), which was obtained using a focusing lens with a focal length of 60 mm. No SH emission had been detected when the fundamental light passed through the crystal in any direction far from the top face. This is consistent with the fact that phase-matched SHG is prohibited in the bulk of BaTiO₃ crystal. Also, no comparable SHG has been detected from the other five faces of the same crystal. The full width at half maximum of the SH peak in Fig. 2(a) is equal to 80 μm .

The SH emission appeared to be localized in the xy plane of the top face of the crystal coming out of the top face within a wide (almost 180°) angle. This peculiar spatial distribution of SHG is illustrated in Fig. 3 which shows a pattern of SH illumination on the screen placed just behind the crystal in the xz plane. The SH light is vertically polarized. Its intensity is proportional to the square of the fundamental light intensity and depends strongly on the polarization state of the linearly polarized fundamental light [Fig. 2(b)]. The SH intensity is approximately 6 times stronger in the case of fundamental light linearly polarized perpendicular to the optical axis of the BaTiO₃ crystal.

All features of the observed SH emission are consistent with the proposed surface SHG enhancement due to the photorefractive surface wave excitation in BaTiO₃. The crystal cut allows photorefractive SEW propagation only on the top face of the crystal (only near this face can photorefractive self-bending and total internal reflection compete with each other). This is consistent with the observation of SHG only from the top face of the crystal. At the same time, the full width at half maximum of the vertical position dependence of SHG in Fig. 2(a) corresponds to the observed range of photorefractive SEW launching in BaTiO₃ [3].

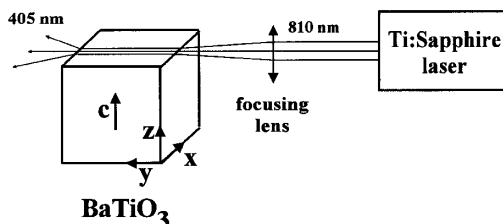


FIG. 1. Schematic view of our experimental geometry.

An explanation of the angular distribution of the observed SHG needs a more detailed analysis. Nonlinear SEW solutions of the Maxwell equations in a photorefractive medium may be found as follows [2]. It is assumed that a SEW written as $E(z, y) = E(z) \exp(-iky)$ induces a dielectric constant change of the form $\epsilon(z) = \epsilon + \delta\epsilon(z)$ due to the photorefractive effect [here $E(z)$ is supposed to be real, ϵ is the real dielectric constant of the medium in the absence of the wave, the photorefractive medium is supposed to be optically isotropic, and the field distribution is assumed to be independent of x . These simplifying assumptions may not be true in the most general case, but they allow us to illustrate the basic physics of the phenomenon]. Substituting this into Maxwell's equations results in the following equation for $E(z)$:

$$[d^2/dz^2 + (k_0^2 - k^2) + k_0^2 \delta\epsilon(z)/\epsilon]E(z) = 0, \quad (1)$$

where $k_0 = \omega(\epsilon\epsilon_0\mu_0)^{1/2}$ is the wave number of the light in a linear medium with the same unperturbed dielectric constant ϵ . Assuming the diffusion mechanism for nonlinearity [11], the distribution $\delta\epsilon(z)$ may be related

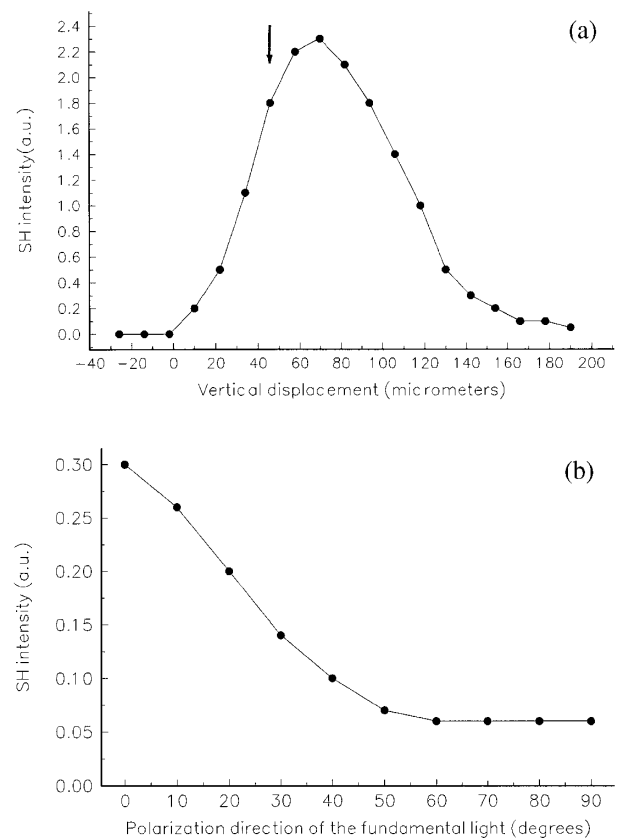


FIG. 2. (a) SH intensity as a function of the vertical position z of the crystal. Large positive z corresponds to the fundamental light passing through the crystal. Approximate position of the focal spot of the lens is shown by the arrow. (b) SH intensity as a function of the polarization direction of the linearly polarized fundamental light, 90° corresponds to the polarization direction parallel to the optical axis of the BaTiO₃ crystal (z direction).

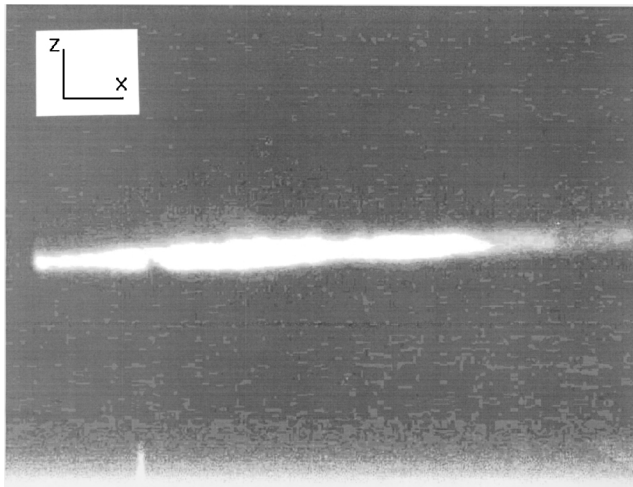


FIG. 3. The pattern of SH illumination produced on a screen placed just behind the crystal. A bandpass filter is used to cut off the illumination by fundamental light.

to $E(z)$ through the space-charge electric field E_{sc} :

$$E_{sc} = -(k_B T/e)[dI(z)/dz]/I(z), \quad (2)$$

where $I(z)$ is the intensity of light. The space-charge electric field induces refractive index changes via the electro-optic effect [11]:

$$\delta\epsilon(z) = 2n^4 r(k_B T/e)[dE(z)/dz]/E(z), \quad (3)$$

where r is the linear electro-optic coefficient. Thus, we obtain the wave equation in the form

$$[(d^2/dz^2)/k_0^2 + (2\gamma d/dz)/k_0 - 2(k - k_0)/k_0]E(z) = 0, \quad (4)$$

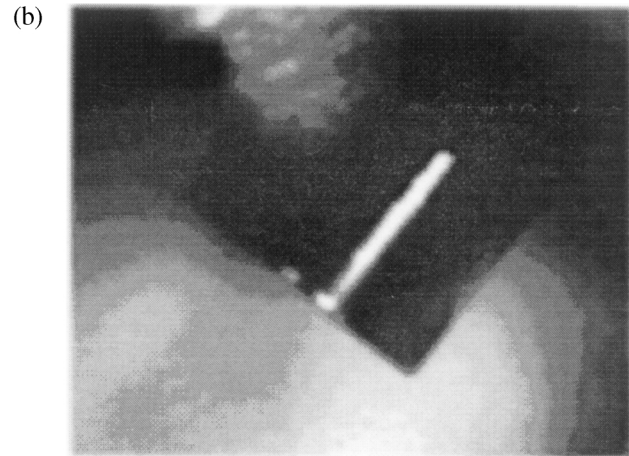
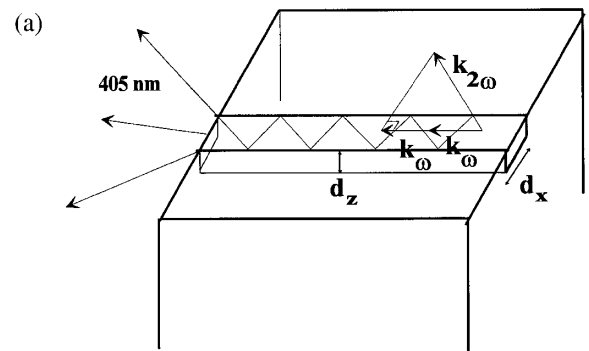
where $\gamma = k_0 n^2 r(k_B T/e)$. This equation has a solution exponentially decaying into the photorefractive medium:

$$E(z) = \exp(-\gamma k_0 z) \cos\{[2(k - k_0)k_0]^{1/2} z + \phi\}. \quad (5)$$

In the case of BaTiO₃ the photorefractive SEW field penetration depth is $d_z = (\gamma k_0)^{-1} \sim 10 \mu\text{m}$ [2]. Since the resulting equation (4) is linear, this penetration depth does not depend on the field intensity.

Real laser beams have finite width in x , but if the width of the beam is much larger than d_z the simplified theory described above should be applicable. Thus, a real life photorefractive SEW must have a localization length in the x direction (d_x) much larger than d_z . Indeed, this is evident from the profile of the photorefractive SEW in BaTiO₃ measured in [3], where $d_x \sim 500 \mu\text{m}$. Unlike d_z , d_x may depend on the intensity of SEW.

A very fruitful approach to all phenomena related to spatial solitons is the representation of solitons as linear waves propagating in the self-induced optical waveguides [12,13]. Let us follow this way of thinking and consider fundamental light propagating in a surface waveguide with a rectangular $d_z \times d_x$ profile such as $d_x \gg d_z \sim 10 \mu\text{m}$ [Fig. 4(a)] (this is an approximation since such a self-induced waveguide does not have sharp physical boundaries, but this approximation works fine for spatial



5 mm

FIG. 4. (a) Phase-matched SHG in the self-induced surface waveguide. (b) A picture of the top face of the crystal taken through the bandpass filter which cuts off the fundamental illumination light. Simultaneous weak illumination with the white light from the flashlight allows the edges of the BaTiO₃ crystal to show. The focused fundamental beam was coming from the top right corner of the image. The surface beam of SH light trapped by the propagating photorefractive SEW is clearly visible.

solitons). The phase matching conditions for SHG in the surface waveguide are further modified. Only the momentum component parallel to the waveguide direction must be conserved. At the same time, such a waveguide is highly multimode with many optical modes corresponding to geometrical optics rays propagating in a zigzag manner parallel to the surface. Thus, there will always be a SH waveguide mode phase matched with the fundamental light. Upon resonant excitation, such a mode will be coupled to many other modes existing in the waveguide at the same frequency. As a result, when the SH light reaches the edge of the crystal, it leaves the surface waveguide in a ray fan parallel to the face of the crystal. This results in the pattern of SH illumination detected in Fig. 3.

We have performed further experiments to confirm the physical picture of the phenomenon described above. Using a 3.6-mm focal length 40 \times microscope objective as a focusing lens in Fig. 1, we have observed much brighter surface SH emission with an average power on the order

of some tens of microwatts. No damage to the surface of the BaTiO₃ crystal was apparent after this experiment. Thus, as much as 10⁻² of the fundamental light power had been converted into SH emission. This is a much higher conversion efficiency than is usually observed in surface SHG experiments: simple calculations show that as much as 10⁷ second harmonic photons per 1 nJ laser pulse have been generated. This is 3 orders of magnitude higher than the conversion efficiency observed in the case of surface SHG enhanced by a surface plasma wave [14]. It is comparable (just an order of magnitude smaller) with the best SH conversion efficiencies obtained in any other experimental geometry. At such a high power self-pumped phase conjugation builds up with the laser power dependent time constant on the order of a few hundreds of milliseconds, causing instability of the Ti:sapphire laser. So, optical isolation is necessary for SHG to be stable (which itself exhibits a similar characteristic buildup time following sudden changes in optical alignment).

A picture of the top face of the crystal taken through the bandpass filter (which cuts off the fundamental excitation light) is shown in Fig. 4(b). Simultaneous weak illumination with the white light from a flashlight allows us to show the edges of the BaTiO₃ crystal. The focused fundamental beam was coming from the top right corner of the image. The surface beam of SH light trapped by the propagating photorefractive SEW is clearly visible. The beam starts from the focal point of the microscope objective. It is possible to see the SHG because of surface scattering. The width of the self-induced surface waveguide is estimated to be on the order of 400 μm.

The polarization properties of SH emission mostly reflect the properties of the second harmonic polarization tensor $d_{ijk}^{(2)}$ of BaTiO₃, which relates SH and the fundamental excitation light ($P_i^{(2)} = \epsilon_0 d_{ijk}^{(2)} E_j^{(1)} E_k^{(1)}$). For a surface SH process in the geometry of our experiment only two nonzero components of $d_{ijk}^{(2)}$ are available: $d_{zxx}^{(2)} = -18.8 \times 10^{-12}$ m/V and $d_{zzz}^{(2)} = -7.1 \times 10^{-12}$ m/V [15]. Thus, the ratio of SH intensity for excitation with fundamental light linearly polarized in the x (horizontal) and z (vertical) directions should be $(d_{zxx}^{(2)}/d_{zzz}^{(2)})^2 = 7.0$ which is very close to the ratio observed in the experiment [Fig. 2(b)].

At the same time, the photorefractive coupling constant r is smaller in the case of horizontally (ordinary) polarized light. This means that the photorefractive SEW field penetration depth d_z is bigger in this case and the fundamental excitation light spends more time away from the surface. According to the simple self-induced waveguide model described above, we should expect stronger attenuation of SHG under these circumstances. In order to account for this discrepancy a complimentary point of view on the nature of SHG enhancement due to the photorefractive SEW excitation may be suggested. In the picture of a SEW as a beam undergoing a cycle of photorefractive deflections towards the face of the crystal and total internal reflections,

a periodic self-induced modulation of the refractive index near the surface of BaTiO₃ crystal may be expected. Such a situation would closely resemble the geometry of SHG experiments with periodically poled nonlinear crystals such as lithium niobate, which show substantial enhancement of SHG efficiency (periodic poling creates periodic modulation of refractive index near the interface).

In conclusion, we have observed strongly enhanced surface SHG in BaTiO₃ due to the excitation of a photorefractive surface electromagnetic wave. The surface SH intensity may reach 10⁻² of the incident fundamental light intensity. A physical picture of this SHG has been introduced that assumes phase-matched SHG in the self-induced surface waveguide. Peculiar angular, crystal orientation, and polarization dependencies of this SHG are presented. They may account for anomalous SHG in BaTiO₃ recently reported in the literature. The observed phenomenon may have many potential applications in nonlinear surface spectroscopy. Also, it may be considered as an example of guiding of light with light in a self-induced surface waveguide, which may find applications in such emerging soliton related techniques as writing virtual photonic circuits [16], etc.

-
- [1] *Surface Polaritons*, edited by V. M. Agranovich and D. L. Mills (North-Holland, Amsterdam, 1982); H. Raether, *Surface Plasmons*, Springer Tracts in Modern Physics Vol. 111 (Springer, Berlin, 1988).
 - [2] G. S. Garcia Quirino, J. J. Sanchez-Mondragon, and S. Stepanov, *Phys. Rev. A* **51**, 1571 (1995).
 - [3] M. Cronin-Golomb, *Opt. Lett.* **20**, 2075 (1995).
 - [4] B. Crosignani, P. Di Porto, M. Segev, G. Salamo, and A. Yariv, *Riv. Nuovo Cimento* **21**, 1 (1998).
 - [5] Y. Kawata, C. Xu, and W. Denk, *J. Appl. Phys.* **85**, 1294 (1999).
 - [6] *Handbook of Lasers with Selected Data on Optical Technology*, edited by R. J. Pressley (CRC Press, Cleveland, OH, 1971), p. 509.
 - [7] W. E. Torruellas, Z. Wang, D. J. Hagan, E. W. VanStryland, G. I. Stegeman, L. Torner, and C. R. Menyuk, *Phys. Rev. Lett.* **74**, 5036 (1995).
 - [8] E. V. Bursian, V. G. Zaleskii, A. A. Luzhkov, and V. V. Maslov, *JETP Lett.* **64**, 270 (1996).
 - [9] L. D. Rotter, D. L. Kaiser, and M. D. Vaudin, *Appl. Phys. Lett.* **68**, 310 (1996).
 - [10] O. Auciello, J. F. Scott, and R. Ramesh, *Phys. Today* **51**, No. 7, 22 (1998).
 - [11] M. P. Petrov, S. I. Stepanov, and A. V. Khomenko, *Photorefractive Crystals in Coherent Optical Systems* (Springer, Berlin, 1991).
 - [12] Y. R. Shen, *Science* **276**, 1520 (1997).
 - [13] A. W. Snyder and D. J. Mitchell, *Science* **276**, 1538 (1997).
 - [14] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984), pp. 479–504.
 - [15] F. Zernike and J. E. Midwinter, *Applied Nonlinear Optics* (Wiley, New York, 1973).
 - [16] A. W. Snyder and F. Ladouceur, *Opt. Photonics News* **10**, No. 2, 35 (1999).