Giant Enhancement of Surface Second Harmonic Generation in BaTiO$_3$ due to Photorefractive Surface Wave Excitation.

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We report observation of strongly enhanced surface SHG in BaTiO$_3$ 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.

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Linear surface electromagnetic waves (SEW) such as surface plasmons or surface polaritons 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 $\epsilon$, 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. 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 and observed experimentally in BaTiO$_3$. This phenomenon is closely related to self-trapped optical beams (also known as spatial solitons) and self-bending beams observed in photorefractive crystals. A photorefractive SEW occurs when a beam self-bends 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 micrometers into the crystal. As a result, a linear 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 topographical defects or by the probe tip of a scanning probe microscope (the field enhancement by a probe tip is discussed in the context of a feasibility study of molecular resolution fluorescence near-field microscopy using multi-photon absorption by Kawata et al. [8]).

In this letter we report the first observation of strongly enhanced surface SHG due to the photorefractive SEW excitation in BaTiO$_3$. Surface SHG in BaTiO$_3$ is a very suitable phenomenon for demonstrating the potential of photorefractive SEWs in nonlinear surface optics. Phase-matched optical SHG (collinear or non-collinear) is forbidden in the bulk of BaTiO$_3$ 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. The momentum conservation law cannot be satisfied in the volume SHG process. Thus, in contrast to experiments done with KTP crystals, observation of the fundamental and phase-matched SHG fields mutually trapped in the volume spatial solitary wave is impossible in BaTiO$_3$. 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 strong photorefractivity of BaTiO$_3$ 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 BaTiO$_3$ reported recently by a number of groups. 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 (NVFRAM) and dynamic random-access memory (DRAM) devices. SHG has been used to determine the crystallographic orientation and the degree of poling of these films (in particular, BaTiO$_3$ films in [9]).
Our experimental geometry is shown in Fig. 1. The iron doped crystal of BaTiO$_3$ 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 2 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 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 it is evident from Fig. 2, 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 BaTiO$_3$ 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 is equal to 80 $\mu$m.

The SH emission appeared to be localized in the plane of the top face of the crystal coming out of the top face within a wide (almost 180 degrees) angle. This peculiar spatial distribution of SHG is illustrated in Fig. 4 which shows a pattern of SH illumination on the screen placed just behind the crystal. 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. 3). The SH intensity is approximately 6 times stronger in the case of fundamental light linearly polarized perpendicular to the optical axis of the BaTiO$_3$ crystal.
All features of the observed SH emission are consistent with the proposed surface SHG enhancement due to the photorefractive surface wave excitation in BaTiO$_3$. 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 SHG in the surface waveguide are further modified. Only the simplified theory described above should be applicable. Thus, a real life photorefractive SEW must have a localization length in the direction of the beam is much larger than $d_z$.

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 $x$ direction ($d_x$) much larger than $d_z$. Indeed, this is evident from the profile of the photorefractive SEW in BaTiO$_3$ measured in [3], where $d_x \sim 50 \mu m$. 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 $d_x >> d_z \sim 10 \mu m$ (Fig.5). 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 zig-zag 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 ray fan parallel to the face of the crystal. This results in the pattern of SH illumination detected in Fig.4.
We have performed further experiments to confirm the physical picture of the phenomenon described above. Using a 3.6-mm focal length 40× 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 BaTiO$_3$ crystal was apparent after this experiment. Thus, as much as $10^{-7}$ 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 $10^7$ second harmonic photons per 1 nJ laser pulse have been generated. This is three 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.6. Simultaneous weak illumination with the white light from a flashlight allows us to show the edges of the BaTiO$_3$ 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 $d^{(2)}_{ijk}$ of BaTiO$_3$, which relates SH and the fundamental excitation light ($P^{(2)}_i = c_0 d^{(2)}_{ijk} E^{(1)}_j E^{(1)}_k$). For a surface SH process in the geometry of our experiment only two non-zero components of $d^{(2)}_{ijk}$ are available: $d^{(2)}_{xxz} = -18.8 \times 10^{-12} m/V$ and $d^{(2)}_{zzz} = -7.1 \times 10^{-12} m/V$ [13]. Thus, the ratio of SH intensity for excitation with fundamental light linearly polarized in the $x$ (horizontal) and $z$ (vertical) directions should be $(d^{(2)}_{xxz}/d^{(2)}_{zzz})^2 = 7.0$ which is very close to the ratio observed in the experiment (Fig.3).

At the same time, the photorefractive coupling constant $r$ is smaller in the case of vertically (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 this 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 BaTiO$_3$ 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 BaTiO$_3$ due to 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 BaTiO$_3$ 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.

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