Intensity Dependence of Optically Encoded Second-Harmonic Generation in Germanosilicate Glass: Evidence for a Light-Induced Delocalization Transition

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Experiments on the ir intensity dependence of the preparation process for second-harmonic generation in germanosilicate fibers and preforms reveal that a sharp threshold of the order of 5 GW/cm^2 exists. The results are explained in terms of a charge-delocalization transition which occurs due to the renormalization of the disorder energy between localized states dressed by an intense nonresonant light field.

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In 1981 Sasaki and Ohmori reported a 10^{-3} conversion efficiency for the second harmonic of a neodymium-doped yttrium-aluminum-garnet (Nd:YAlG) laser operating at 1.06 μm in a centrosymmetric silica-based optical fiber.[1] Following this discovery, the problem was brought to the forefront of nonlinear optics when Osterberg and Margulis reported a 5% conversion efficiency which evolved over a period of hours in a phosphorous-codoped germanosilicate fiber.[2-4]

After nearly five years, the basic physics of this phenomenon is still a mystery. The two central issues are the origin of the nonlinear response and the way in which the material self-organizes to produce phase-matched nonlinear optical interactions.

Detailed calculations by Terhune and Weinberger of the second-harmonic generation (SHG) possible in centrosymmetric silica glass revealed that these effects could at most result in a 10^{-10} conversion efficiency under phase-matched conditions.[5] Based on these estimates, several groups postulated that intrinsically noncentrosymmetric color centers or defects within the fiber core were aligned periodically to form a $\chi^{(2)}$ grating which resulted in quasi-phase-matched frequency doubling.[6,7]

This model was initially believed to be correct after Stolen and Tom showed that fibers containing Ge as a dopant could be prepared in minutes when both the fundamental and the second harmonic were simultaneously introduced into the fiber.[7,8] This process, referred to as seeded preparation, was believed to be due to the encoding of defect orientation by the periodic optical rectification field which results from a $\chi^{(3)}(0;\omega,\omega,-2\omega)$ mediated interaction of the fundamental and the second harmonic. Unfortunately, the dc fields associated with optical rectification in the silica are of the order of 1 V/cm resulting in orientation interaction energies of the order of $10^{-6}kT$. Although experimental tests of this model in fibers have revealed that fields as large as 10^3 V/cm have no effect,[9] it does explain most of the features of the resultant phase-matching grating.[10] Since the development of the defect orientation models, other theories have evolved which rely on charge-related effects.[11,12] These models, however, result in conversion efficiencies which are at least 4 orders of magnitude too small and in some cases violate the symmetry requirements consistent with the observed modal structure in fibers.

The results on electric-field poling with blue-light excitation (488 nm) indicate that with fields of the order of 5×10^6 V/m excited carriers can be swept aside and retrapped in energetically deep states.[13] The most likely transitions responsible for this effect are associated with the two-photon excitation of electrons from oxygen-deficient sites such as ≡Ge−Si≡, ≡Ge−Ge≡ bonds or electron traps such as Ge(I) and Ge(II). The excited electrons are most likely to rapidly recombine with the emission of a photon and the hole may hop by phonon-assisted processes. The importance of the latter mechanism in seeded preparation of fibers has been tested in low-temperature (77 K) experiments where weak (factor of 5 in the rate of $\chi^{(2)}$ evolution) or no noticeable change in the time evolution or final conversion efficiency were found.[14,15] In view of the expected 10^4-10^5 increase in SHG growth rate for a variable-range-hopping mechanism these results give further evidence that diffusive electronic transport models are not a likely explanation for SHG in germanosilicate fibers.

Experiments were performed to study the onset of second-harmonic generation in various germanosilicate fibers and bulk preforms as a function of the peak intensity of the fundamental. The fiber preparation experiments utilized a cw mode-locked Nd:YAlG laser (76 MHz) operating at 1.06 μm with pulses of 110 and 80 ps duration at the fundamental and the second harmonic, respectively. The average power exiting the fiber at 532 nm in the fiber was maintained at a constant value of 8 mW while the ir power was varied using crossed polarizers. All of the experiments were performed without separating the fundamental and second-harmonic beams in order to avoid thermal phase-fluctuation effects, and a final fixed polarizer for maintaining the polarization of the beams. The second-harmonic and ir powers were controlled by rotating the potassium-titanyl(II)-phosphate (KTP) crystal to control the relative power of the two beams. The experimental setup is shown in Fig. 1. The fiber segments (10 and 30 cm long) were prepared for twenty minutes at each intensity. Exposure time measurements as long as several hours on various fibers

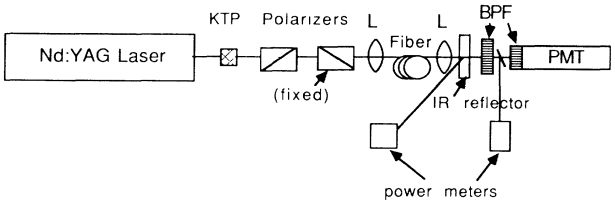

FIG. 1. Experimental setup for fiber experiments: L denotes coupling lenses, BPF denotes bandpass filter (532 nm), and PMT denotes photomultiplier tube.

used in these experiments revealed that the final conversion efficiency saturated after approximately five minutes, indicating that twenty minutes of preparation time is adequate to reach a steady state.

The experiments were performed on various germanium-doped fibers, all of which were single mode at 1.06 μm. One of the fibers had a single-mode cut off at 630 nm and the others contained either phosphorus or neodymium as a codopant. The second-harmonic beam was coupled into the LP_{01} mode of all the fibers. The resulting second-harmonic output was measured using a phase-sensitive detection system capable of resolving less than 1 pW of average power at 532 nm. Measurements were made on new strands as well as by successive preparation of the same fiber, and no difference was observed in the saturated SHG vs ir preparation behavior.

Experiments on reading the fiber at the preparation value as opposed to a fixed value showed no significant difference, indicating that nonlinear index and thermal-index effects do not play an important role. This finding is in agreement with the fact that n_2 for silica is about 10^{-16} cm^2/W, leading to index changes of the order of 10^{-6} and coherence-length changes of the order of 0.4%. Furthermore, the absorption of ir light in our fiber leads to temperature increases of the order of 0.1 °C. This temperature increase along with the dispersion in dn/dt leads to negligible thermally induced phase-matching effects.[11]

Figure 2 shows the output, read at the same ir value, from various fibers as a function of transmitted ir peak intensity used to prepare them. The results indicate that most fibers show an increase of several (5–8) orders of magnitude over a region of about 0.5 GW/cm^2 with final conversion efficiencies of the order of 10^{-3}–10^{-2}. Certain fibers were found to exhibit exceptionally narrow transition regions which are less than 5% wide in ir peak intensity. The general behavior shown in Fig. 2 was observed in several hundred fibers without exception.

It is important to note that the longer fibers (30 cm) always showed an apparently lower critical intensity for the sharp increase in second-harmonic generation. This results from the measurement of the transmitted ir power in the fiber which is strongly affected by leaky mode effects.[16] Fiber cutback experiments show that apparent attenuation coefficients as large as 5×10^{-2} cm^{-1} can result. The lower apparent preparation values for

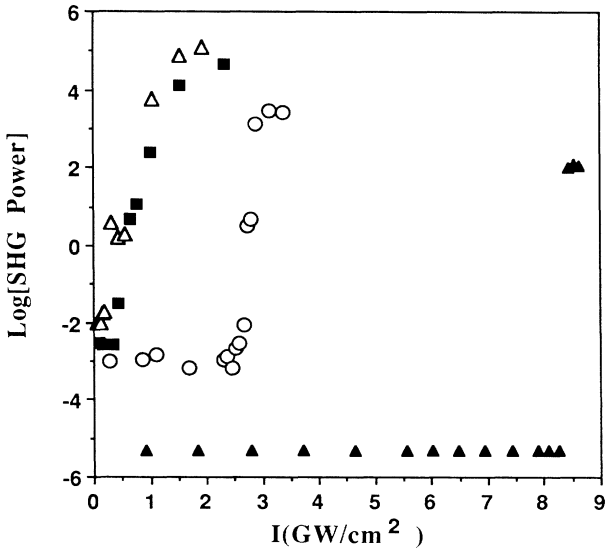

FIG. 2. A log-linear plot of the saturated second-harmonic signal from several fibers as a function of the transmitted ir intensity used during preparation. The fibers were prepared with a constant value of 8-mW average power at the second harmonic. The fibers were all illuminated with the same value of ir to obtain the second-harmonic signal. The open triangles represent a 3% Ge- and 0.5% P-doped fiber 30 cm long, the squares represent a 30-cm piece of 2% Ge- and 10^{-2}% Nd-doped fiber, the circles represent a 10-cm-long segment of the same fiber, and the solid triangles represent a 10-cm-long piece of 5% Ge-doped fiber single mode at 630 nm. The P- and Nd-doped fibers were manufactured by T. F. Morse's group at Brown University, and the 630-nm cutoff fiber was purchased from Radiant Communications (SM-6).

30-cm-long segments of P-codoped and Nd-codoped fibers represented by the open triangles and the squares, respectively, in Fig. 2 are consistent with a previous measurement on a 50-cm strand.[17] With the exception of the Radiant Communications fiber, the sharpness of SHG vs ir preparation power was approximately the same for the long and short pieces, but the value at which it occurs shifted.

Finally, we compared the growth of the second-harmonic power over the background value using cw and mode-locked operation of the laser. In the case that the ir and second-harmonic average powers are equal, all the *intensity-independent material response* models with holographic encoding predict that the mode-locked case should result in a second-harmonic output which is larger by the duty cycle of the mode-locked laser ($\sim$140) when the prepared fibers are read under the same conditions (mode-locked ir). This is because lower powers are compensated for by the continuous action of the fields. Two fibers (Corning Coreguide, 8-μm core, 5% Ge and the fiber with Nd doping referred to earlier) were studied with the same setup used for the preparation experiments. The average powers transmitted through the fibers were 8.5 W and 5 mW for the ir and green, respectively, and both were coupled into LP_{01}.

After half an hour the mode-locked preparation resulted in an increase of $\sim 10^8$ while the cw preparation increased by 300 for the Nd fiber. The Corning fiber exhibited no increase due to cw preparation but increased by 10^4 with mode-locked preparation. These results show that, even if the mode-locked case had resulted in greater two-photon erasure and saturated, the intensity-independent models for this process are off by 3 to 4 orders of magnitude (for $\chi^{(2)}$).

In addition to the experiments on fibers, the preparation of a preform with 5.2-wt% Ge- and 0.5-wt% P-doped silica core region was accomplished using Q-switched and mode-locked operation of the Nd:YAlG laser.[18] The 1.5-cm-long preform section was exposed to ir pulses with peak intensities of the order of 5 GW/cm^2, the same typical value used in the fiber experiments. The experiments indicated that a sharp threshold exists for the preform as well, and that the second harmonic grows by 10^5 over approximately 1 W of average ir power. This result is important because of the absence of any complications introduced by fiber modes.

The appearance of a rapid increase in SHG power has not been seen by Kamal and Weinberger, who observe behavior consistent with the intensity-independent material response models for fibers that exhibit a maximum conversion efficiency of 10^{-5}.[19] Others, however, have seen that self-preparation does not evolve until a critical value of ir intensity is exceeded, even for fibers with very different initial internal SHG generation.[20]

The sharp ir power dependence observed in the experiments corresponds to peak intensities of the order of 5 GW/cm^2 and is expected to affect the relative energies of bound states. A simple calculation of the shift in energy-level separation of a two-level system dressed by an intense nonresonant field ($h\nu \gg \Delta E_0$) shows that the energy-level separation becomes renormalized and is given by[21]

$$\Delta E(\varepsilon_0) = \Delta E_0 \{1 - [\bar{\mu}_{ij}\bar{\varepsilon}_0/\hbar\omega]^2\}. \quad (1)$$

ΔE_0 is the unperturbed energy separation, μ_{ij} is the matrix element, and ε_0 is the electric-field amplitude of the plane wave of frequency ω.

An interesting case occurs when the matrix element is associated with two spatially separated, localized electronic states such as the midgap states in Ge-doped silica. In such systems the wave functions may overlap but the electron or hole is localized by the energy and off-diagonal disorder. The overlap of the wave functions results in a bandwidth which is too small to trigger the onset of quantum transport. The classic work by Anderson has shown that when the disorder energy sufficiently exceeds the energy bandwidth, localization of electrons occurs.[22] In the presence of an intense nonresonant field, the average spread in the energy between localized states is expected to decrease due to renormalization by the photon field. When the Anderson criterion (disorder energy less than energy bandwidth) is no longer fulfilled, the optically dressed system is expected to exhibit delocalized electronic states.[23]

An estimate of the critical intensity can be made by considering only the dominant nearest-neighbor interactions to approximate μ_{ij} and the transfer-matrix element which, in the tight-binding limit, accounts for the bandwidth of the system. Assuming an exponential dependence for the localized state wave function with a decay length β^{-1} and an average separation between sites R, the dipole matrix element and the bandwidth (δ) are approximately given by[24]

$$\mu_{ij} \approx e[R(1+\beta R)/2]e^{-\beta R}, \quad (2)$$

$$\delta = \frac{e^2\beta[3/2(1+\beta R)+1/6(\beta R)^2]}{2\pi\varepsilon} e^{-\beta R}. \quad (3)$$

Using a value of $\beta^{-1} = 15$ Å and $R = 35$ Å, we arrive at values of $\mu_{ij} \sim 30$ D and $\delta \sim 0.2$ eV. The value of β is a function of the excitation state of the defect and is generally smaller if the center is optically excited.

The critical intensity required for delocalization may be estimated by applying the Anderson criteria [$\Delta E(\varepsilon_0) < z\delta$]. The result is given by

$$I_c \approx \frac{c\varepsilon}{2n(\omega)} \left[\frac{h\omega}{\mu_{ij}}\right]^2 \left[1 - \frac{z\delta}{\Delta E_0}\right], \quad (4)$$

where z is the connectivity factor for the system ($z \sim 4$), $n(\omega)$ is the index of refraction, and ΔE_0 assumes a value of the order of the width of the random energy-level distribution which, for the Ge(N) defects, is of the order of 1 eV.[25] Substitution of the values for the parameters results in $I_c \sim 10^{10}$ W/cm^2 when $1 - z\delta/\Delta E_0 \sim 10^{-2}$. This value, however, is extremely sensitive to the localized site separation which controls μ_{ij} and δ. In addition, no account of possible electron correlation effects has been included.

The theoretical estimate given indicates that about a critical optical intensity electrons in localized midgap states may become delocalized when the system is near percolation. The possible connection between this effect and SHG in germanosilicate glasses rests on how charge delocalization can lead to the creation of an effective second-order nonlinearity and phase matching. Recent experiments have shown that the $\chi^{(2)}$ grating-formation process requires temporal simultaneity of fundamental and the second-harmonic fields.[26] The simultaneous application of both the fundamental and harmonic fields is expected to result in (1) optical renormalization of the energy differences between localized states resulting in delocalized midgap states (due to the intense ir); (2) the combined action of two fields with the electron to shift the center of charge via local nonlinear potential terms (both ir and second harmonic); and (3) single and two-photon excitation of trapped electrons to states near the mobility edge of silica due to the second-harmonic intensity.

The local displacement of the electron from the center

of charge due to the combined action of the fields at ω and 2ω depends on their relative phase and the polarizability of this state. Since this local displacement can be cast in terms of an induced quasistatic dipole moment, we can replace the nonlinear interaction of the fields in terms of an effective dc field acting on the electron. The effective dc field is given by

$$E_{\mathrm{dc}} \approx \left[\frac{\gamma(0;\omega,\omega,-2\omega)}{\alpha}\right] E^2(\omega)E^*(2\omega)e^{i\{k(2\omega)-k(\omega)\}z}. \quad (5)$$

Here, $E(\omega)$ and $E(2\omega)$ are the amplitudes of the fundamental and second-harmonic fields, respectively, $k(2\omega)$ and $k(\omega)$ are the wave vectors of the second-harmonic and fundamental waves, respectively, α is the dc linear polarizability, and $\gamma(0;\omega,\omega,-2\omega)$ is the third-order molecular polarizability. In three dimensions, the polarizabilities γ and α are expected to scale as R_0^7 and R_0^3, where R_0 is the localization length of the electronic state.[27,28]

In the absence of the optical delocalization effect described, $R_0 \sim 5$ Å and the intrafiber fields result in center of charge shifts equivalent to those produced by the dc fields of the order of 1 V/cm. However, *as the charge-localization length increases due to the optical renormalization of the disorder energy, R_0 becomes large and the effective dc field and the displacement grow rapidly.* Based on the experimental observation that dc fields of the order of 10^4 V/cm have produced measurable effects, the nominal extent of the delocalized states which result due to the optical process described must be of the order of 20–40 Å. This value implies that the process could be limited to charge transfer of an electron between two neighboring sites during delocalization. The most likely sites are expected to be Ge(I) traps which exhibit an anomalously large linewidth in their 281-nm absorption.[25] Furthermore, the rupture of $\equiv$Ge$-$Si$\equiv$ bonds as well as the excitation of the electrons in the blue region of the spectrum to states above the mobility edge will result in charge redistribution and the erasure of the dc field producing the effective $\chi^{(2)}$ grating.[29]

The directional electron-transfer mechanism described will result in a periodic frozen-in dc field associated with the creation of a space-charge field which can result in phase-matched electric-field-induced SHG. The measured $\chi^{(2)}$ values, assuming periodic phase matching for germanium- and phosphorus-doped fibers, are of the order of 10^{-15}–10^{-14} m/V. This value along with the $\chi^{(3)}$ of silica implies that a local frozen-in static electric field of the order of 10^7 V/m exists. Such a field requires an electron density of the order of 10^{18}/cm^3, assuming a retrapping distance of 35 Å, and 10^{13}/cm^3 if the charges migrate across the core (~ 1 μm). Further tests of this model based on magnetic-field modification of the localized electron wave function are currently in progress.

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