Frequency Upconversion of 800 nm Ultrashort Pulses by Two-Photon Absorption in a Stilbenoid Compound-Doped Polymer Optical Fiber**

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We present the results of a study of frequency upconversion of femtosecond optical pulses in a step-index polymer optical fiber that uses a stilbenoid compound as an active dopant. Intense blue emission is observed in the doped poly(methyl methacrylate) (PMMA) fiber when it is longitudinally pumped at 800 nm by 175 fs optical pulses. By means of the intensity-dependent transmission method, the two-photon absorption cross-section is deduced. Our study illustrates that the combination of a well-designed organic chromophore incorporated into a fiber geometry is appealing for the development of an upconversion blue polymer laser.

1. Introduction

Compact, lightweight, inexpensive lasers operating in the blue spectral region are desired for use in such diverse applications as medical diagnostics, surgery, high-capacity optical storage, and high-resolution scanning and printing. Methods of generating these shorter wavelengths include optical harmonic generation and sum-frequency mixing techniques that require phase matching in expensive inorganic crystals. Alternatively, frequency upconversion by two-photon absorption can be used to generate blue light by pumping in the infrared, and provides an excellent alternative to GaN based technologies.[1]

There have been two major technical approaches to the generation of short wavelength coherent radiation by means of multiphoton absorption-induced emission: 1) sequential step-like absorption of single photons by intermediate metastable states, and 2) simultaneous absorption of photons via virtual states. The first approach has been extensively used for rare earth-doped inorganic crystals[2,3] and glasses.[4–6] Here, we focus on the second approach in which the process can be described by the imaginary part of the third-order susceptibility.

Multiphoton transitions involving the simultaneous absorption of more than one photon were first predicted by Göppert-Mayer[7] in 1931 and were demonstrated in the laboratory in 1961 by Kaiser and Garret[8] for transitions in CaF_2:Eu^{2+} with a ruby laser excitation at 694 nm. Since then, two-photon excited emission has been used to generate coherent radiation. The first two-photon pumped stimulated emission was reported by Patel et al. who demonstrated 6.5 μm radiation from PbTe crystals that were pumped at 10.6 μm.[9] More recently two-photon pumped stimulated emission and lasing have been shown in a variety of gain media. These include semiconductor crystals[10] and organic dyes in solutions,[11,12] solid matrices,[13] and waveguides.[14,15]

The great degree of flexibility in molecular design and chemical synthesis of organic materials gives them several clear technical advantages over other materials under study in this area. The material parameters crucial for the design of efficient light amplification and lasing devices such as absorption and emission wavelengths, photoluminescence quantum yield, bandwidth, Stokes shift, and compatibility with host materials, can be fine-tuned by varying the chemical structure. In addition to this, organic materials are amenable to fabrication processes at relatively low temperatures compared to those of inorganic materials, typically, around 100 °C, which allows a variety of organic chromophores to be incorporated into the host without thermal decomposition. Lastly, their potentially very low cost makes organic materials competitive for industrial applications.

Being a third-order process, the transition probability for two-photon absorption is much less than the transition probability for the absorption of only one photon. Therefore, in order to realize efficient upconversion, it is imperative to design a chromophore with a large two-photon absorption cross-section as well as to employ a device structure that facilitates efficient interaction between pump light and the gain medium. Upconversion by two-photon absorption has the advantage of being angle insensitive, and can thus be incorporated into a waveguide structure. This provides a long interaction length and strong optical confinement, allowing high light intensities to be achieved.

Optical fibers are very flexible, possess a geometry that can be easily integrated into existing lightwave systems, offer output power scalability, and have a high surface-area-to-volume ratio, leading to efficient heat dissipation and minimiza-

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tion of thermal degradation of performance. Despite these attractive features, there has been only one report on upconverted lasing in a polymer fiber configuration. In the pioneering work by He et al., upconverted lasing at 610 nm was demonstrated in a glass-clad dye-doped polymer optical fiber under nanosecond photoexcitation at 1064 nm.[14] A tailor-made dye, trans-4-[*p*-(N-hydroxyethyl-*N*-methylamino)styryl]-*N*-methylpyridinium iodide, incorporated in poly(2-hydroxyethyl methacrylate) was used as the gain medium. The glass-clad fiber was immersed in a liquid cell of suitable refractive index in order to reduce the effects of irregularities at the fiber ends. As poly(2-hydroxyethyl methacrylate) is highly hydrophilic and can swell by absorbing water in ambient atmosphere, the use of PMMA or a copolymer based on PMMA as a fiber material is more appropriate for the fabrication of a doped polymer fiber.

In this contribution, we report on upconverted photoluminescence in an all-polymer fiber for the first time. A novel blue-emitting compound, 1,4-bis(4-diphenylamino-styryl)-benzene (referred to as SP35), was incorporated into a step-index fiber structure. The molecular structure of SP35 is shown in the inset of Figure 1. It has high fluorescence quantum yields of 0.94 in dioxane and 0.85 in polystyrene, and

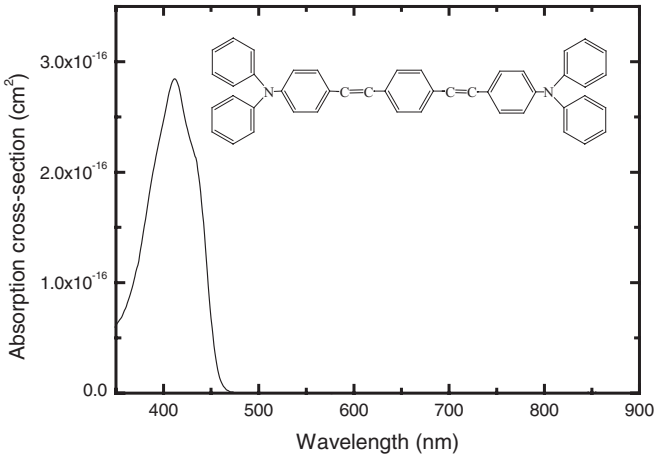

Fig. 1. The single-photon absorption cross-section spectrum of 1,4-bis(4-diphenylamino-styryl)benzene (SP35) in *ortho*-xylene. The inset shows the molecular structure of SP35. No measurable absorption is seen in the near-infrared region.

shows a relatively large Stokes shift of ~50 nm, implying a low re-absorption rate. Moreover, it readily dissolves into monomer solution of the commonly used polymers. We confirmed that SP35 is readily dissolved into methyl methacrylate solution up to about 1 % by weight. After polymerization, the polymer bulk obtained did not show any noticeable light scattering due to aggregation of the compound. Henari et al. reported lasing characteristics of SP35 in toluene in a dye-laser configuration.[16] Also, Kretsch et al. showed distributed feedback lasing from SP35 incorporated into a polystyrene waveguide.[17] Kobayashi et al. have also demonstrated large optical gain and lasing in SP35-doped glass-clad polymer optical fibers.[18,19]

2. Results and Discussion

Figure 1 shows the single-photon absorption cross-section spectrum of the compound. The absorbance of SP35 dissolved in orthoxylene by one parts per million by weight was measured in a 1 cm path length cuvette. The absorption cross-section $\sigma_a(\lambda)$ is given by

$$\sigma_a(\lambda) = -\frac{\ln T(\lambda)}{Nd} \quad (1)$$

where N is the total active dopant concentration, d is the optical path length, and $T(\lambda)$ is the transmission. As can be seen in the spectrum, there is no measurable absorption in the near-infrared region. The broad spectral width is indicative of vibrational manifolds superimposed on the electronic states, common to organic molecules. The absorption spectrum of SP35 indicates a possible two-photon absorption peak in the region of 800 nm. At this wavelength region, PMMA has a relatively low loss window between the absorption peaks due to 4th and 5th harmonics of the C–H vibration.

We used step-index PMMA fibers, with 175 μm core diameter and 350 μm outer diameter, whose cores were doped with 1 wt.-% SP35 and were designed to have a numerical aperture of 0.3.[20] The cutback method was employed to deduce the linear loss of the fibers at 800 nm. The data were assumed to obey the Beer–Lambert law and were fitted to the equation $I(L) = I_0 \exp(-\alpha L)$, where α, L, I_0, and $I(L)$ are the linear loss coefficient, fiber length, launched light intensity, and transmitted intensity from the fiber, respectively. The linear loss coefficient was measured to be 0.013 cm^{-1}, which translates to 5.5 dB m^{-1}. Since the fibers characterized below were only tens of centimeters in length, this linear loss was sufficiently low.

Under the launching conditions described in the Experimental section, upconverted photoluminescence could be readily observed. Figure 2 shows a photograph of the fiber when it was longitudinally pumped at 800 nm by the 175 fs optical pulses. In Figure 3, the two-photon excited emission spectrum from a 20 cm length fiber is shown together with that of the steady-state single-photon excited emission. The single-photon excited emission spectrum was measured for SP35-doped PMMA bulk, photoexcited at 373 nm with a light-emitting diode. The two-photon pumped emission spectrum is centered on 499 nm and has a full width at half maximum (FWHM) of ~60 nm, whereas

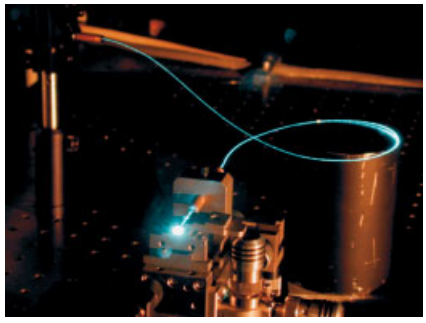

Fig. 2. Upconverted blue emission from the SP35-doped step-index PMMA fiber under longitudinal photoexcitation by 800 nm femtosecond pulses.

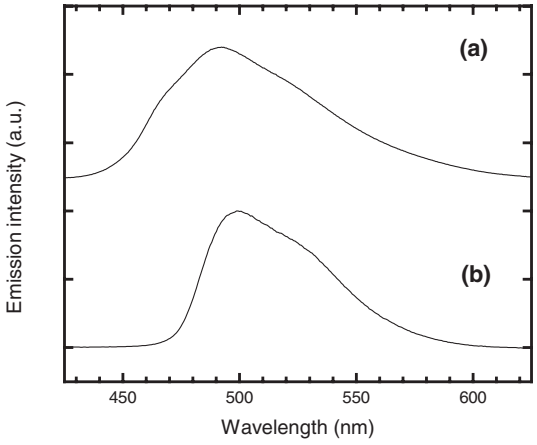

Fig. 3. Emission spectra of the single-photon-pumped emission from a PMMA bulk doped with SP35 (curve (a)), and of the two-photon-pumped emission from the 20 cm fiber (curve (b)). The single-photon excited emission spectrum was measured for an SP35-doped poly(methyl methacrylate) (PMMA) bulk, photoexcited at 373 nm with a light-emitting diode. Curve (b) is the emission spectrum resulting from 20 cm of fiber when longitudinally pumped with 175 fs Ti:sapphire pulses at 800 nm.

the spectrum for single-photon excited spontaneous emission peaks at 492 nm with a FWHM of ~80 nm. The two-photon excited emission spectrum is also slightly red-shifted and narrowed with a less evident higher-energy vibronic shoulder corresponding to the 0–0 transition. This is accounted for by the ground-state self-absorption of a higher energy part of the spectrum by the active dopants as the emitted light travels through the 20 cm fiber. Note that we observed no significant spectral narrowing and hence did not identify the existence of large optical gain expected for the material.

Near-infrared pumped photoluminescence in the visible requires a multiphoton absorption process. In Figure 4, we plot the integrated photoluminescence intensity on a logarithmic scale as a function of launched pump light intensity. A power-law dependence of exponent 2.1 is found, which is indicative of a two-photon excitation process.

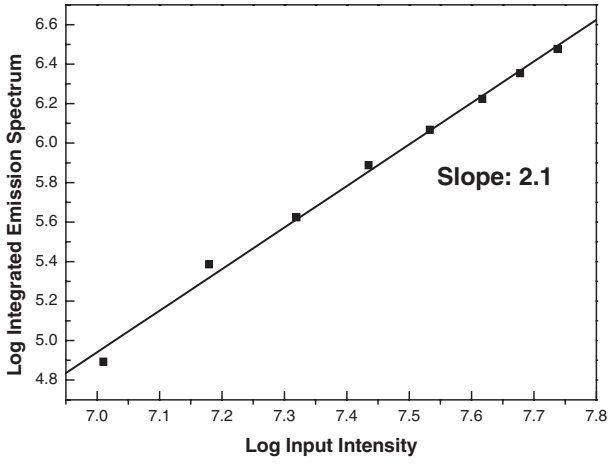

Fig. 4. Logarithmic plot of integrated emission intensity versus input intensity. The emission was measured for a 20 cm fiber longitudinally pumped at 800 nm by 175 fs optical pulses. A power-law dependence of exponent 2.1 is found, which is indicative of a two-photon excitation process.

We performed the intensity-dependent transmission measurements to determine the two-photon absorption cross-section. As the total loss experienced by the light is a sum of linear and nonlinear intensity-dependent absorption, the equation that describes propagation in the presence of linear and two-photon absorption can be written as[21]

$$\frac{dI(z)}{dz} = -\alpha I(z) - \beta I(z)^2 \quad (2)$$

where α is the linear loss coefficient, β is the two-photon absorption coefficient, and I is the light intensity. For the boundary condition $I(0) = I_0$, and a given propagation distance L, this equation is integrated to give

$$I(L) = \frac{I_0 \exp(-\alpha L)}{1+\beta I_0 L_{\text{eff}}} \quad (3)$$

where L_{eff} is the effective length, which is defined as $L_{\text{eff}} = [1-\exp(-\alpha L)]/\alpha$. Thus at sufficiently high intensities, the nonlinear absorption coefficient can be determined directly by measuring the beam attenuation or the decrease in transmission.

In Figure 5, we plotted the inverse transmission,

$$T^{-1} = \frac{I_0}{I(L)} \quad (4)$$

to deduce the linear and two-photon absorption coefficients. The solid curve is fitted to the data using Equation 3. At sufficiently low input intensity, the linear loss coefficient given

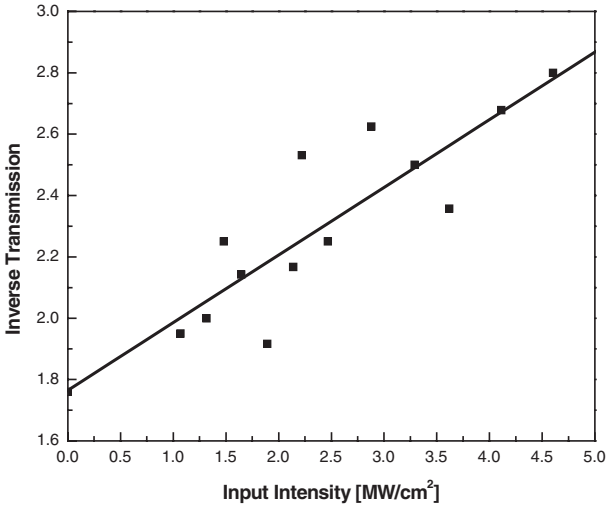

Fig. 5. Inverse transmission as a function of input power. The fiber length was 53 cm. The solid curve is fitted to the data by use of Equation 3. The linear loss coefficient deduced from the intersect is $\alpha = 0.011$ cm^{-1} and the two-photon absorption coefficient obtained from the slope is $\beta = 5.6$ cm GW^{-1}, which translates to $\sigma^{(2)} = 7.8 \times 10^{-19}$ cm^4 GW^{-1} or $\sigma^{(2)} = 1.9 \times 10^{-46}$ cm^4 photon^{-1} s^{-1}.

by the intercept of an inverse transmission versus input intensity plot is 0.011 cm^{-1} at 800 nm. This shows good agreement with the result of the independent loss measurement by use of the cut-back method. The two-photon absorption coefficient is associated with the slope of the line in Figure 5. The resulting two-photon absorption coefficient as calculated from the best fit is 5.6 cm GW^{-1}, which gives a corresponding

value of the two-photon absorption cross-section of $\sigma^{(2)} = 7.8 \times 10^{-19}$ cm^4 GW^{-1} or $\delta^{(2)} = 1.9 \times 10^{-46}$ cm^4 photon^{-1} s^{-1}.

Since the fibers used in the present study have a core diameter of 175 μm and a numerical aperture of 0.3 and are, therefore, highly multimode, we anticipate that femtosecond optical pulses experience broadening effects while propagating in the fiber mainly due to intermodal dispersion, and have temporal widths larger than that of the input pulse at a given point along the propagation direction. In the extraction of the β and $\sigma^{(2)}$ presented above, no effect of pulse broadening was taken into account. This means that we have overestimated the pump light intensity in the core and, in turn, underestimated the two-photon absorption coefficient. Therefore, the values of the two-photon absorption coefficient and the corresponding two-photon absorption cross-section extracted here are considered to be the lower limit of the possible real values. We believe that the two-photon absorption cross-section value obtained for SP35 is among the largest reported to date for this class of materials under femtosecond photoexcitation. It exceeds that of 6.58×10^{-48} cm^4 photons^{-1} s^{-1} reported by Mukherjee et al.[22] for a custom-made dye, AF-50, in PMMA under 200 fs photoexcitation at 800 nm.

3. Conclusions

While use of an active dopant with a large two-photon absorption cross-section and good solubility such as SP35 is important for the design of a compact upconversion lasing device, it is important to incorporate the material into a structure that allows for very efficient interaction between the pump beam and the material. For upconversion to be effective, high intensities must be maintained over long distances. The obvious solution to this is to incorporate the dopant into a fiber which also allows very flexible control of interaction length and dopant concentration. In addition to this, the numerical aperture can be adjusted to optimize the modal structure of both the pump and lasing beams.

Further characterization of ultrashort optical pulse propagation in the fiber and optimization of the host composition and device parameters are in progress in order to realize upconverted lasing.

4. Experimental

In order to characterize the upconversion process, the output from a mode-locked Ti:sapphire laser was launched into the cleaved fiber end by use of a 10 cm focal length lens. Optimal coupling was achieved by mounting the fiber in a micro-positioning fiber holder. The fiber cleave was monitored for damage by use of a charge-coupled device (CCD) camera array. During the course of all experiments, no damage of the fiber end was observed. The upconverted light was collected at the fiber end by use of a short focal length collecting lens and the resulting spectrum was measured on a CCD and monochromator.

The cut-back method was employed to verify a low linear loss in the fiber at 800 nm. The Ti:sapphire laser tuned at 800 nm was used as a light source in the continuous-wave (CW) operation mode. The measurements were carried out in the low intensity regime so as not to induce nonlinear optical effects. The transmission change with fiber length was measured using a laser power meter and was assumed to obey the Lambert–Beer law.

For intensity-dependent transmission measurements, the output from a mode-locked Ti:sapphire laser was launched into the fibers. The details of the pump beam launching and the fiber output detection were as described above.

Throughout repeated experiments, no apparent photodegradation of the dopant was observed.

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