1-1-1991

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W. E. Torruellas

L. A. Weller-Brophy

R. Zaroni

G. I. Stegeman

University of Central Florida

Z. Osborne

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Recommended Citation

Torruellas, W. E.; Weller-Brophy, L. A.; Zaroni, R.; Stegeman, G. I.; Osborne, Z.; and Zelinski, B. J. J., "Third Harmonic Generation Measurement Of Nonlinearities In Sio2-Tio2 Sol-Gel Films" (1991). *Faculty Bibliography 1990s*. 354.

<https://stars.library.ucf.edu/facultybib1990/354>

Authors

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Cite as: Appl. Phys. Lett. **58**, 1128 (1991); <https://doi.org/10.1063/1.104392>

Submitted: 20 September 1990 . Accepted: 13 December 1990 . Published Online: 04 June 1998

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Third-harmonic generation measurement of nonlinearities in SiO₂-TiO₂ sol-gel films

W. E. Torruellas,^{a)} L. A. Weller-Brophy,^{b)} R. Zanoni,^{c)} and G. I. Stegeman^{d)}
Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

Z. Osborne and B. J. J. Zelinski

Materials Sciences and Engineering Department, Arizona Materials Laboratory, University of Arizona, Tucson, Arizona 85721

(Received 20 September 1990; accepted for publication 13 December 1990)

Third-harmonic generation has been used to measure the magnitude and phase of the nonlinear susceptibility $\chi^{(3)}(3\omega)$ of SiO₂-TiO₂ sol-gel thin films as a function of TiO₂ concentration. Nonlinearities 20 times larger than those of fused silica were found, making such films useful for nonlinear optics in glass waveguides.

Glasses in the form of waveguides, both fiber and planar, have recently been used to study various nonlinear optical phenomena such as all-optical switching¹⁻⁴ and spatial solitons.⁵ In particular, Aitchison and co-workers have studied spatial soliton propagation and interactions in planar waveguides fabricated by ion exchange using glasses with nonlinearities as large as 20 times that of fused silica.⁵ Although ion exchange has the advantage that waveguides can be buried reducing damage at surface imperfections, the limited index difference which can be achieved does not allow tight optical confinement.⁶ Waveguides formed by spin coating sol-gels^{7,8} are a possible alternative for forming highly nonlinear glass waveguides with strong confinement. They have been reported to form low-loss (< 1 dB/cm) waveguides whose properties can be tailored,⁷ which can be patterned by embossing⁸ and which are capable of withstanding optical power densities in excess of 10 GW/cm² in nanosecond pulses.⁷ Because of their simple preparation techniques, sol-gel methods are also an easy way to prepare high index glass films in order to investigate their nonlinear properties. They can be helpful in the identification of the components which originate the nonlinearity. High concentration of heavy ions can be obtained for binary sol-gel films. This is rarely the case for bulk glasses, rendering this type of investigation very difficult.⁹ In this letter we report third-harmonic generation (THG) measurements of the electronic nonlinearities of sol-gel waveguide films as a function of TiO₂ concentration.

The sol-gel films were prepared as follows. Tetra-ethyl-ortho-silicate (TEOS) is typically mixed with isopropyl alcohol for 4 min, followed by hydrolysis in 0.5 mol% HCl for an additional 15 min. Titanium butoxide and 2-4-pentabedionate are mixed for 20 min and added to the TEOS solution and the combination is mixed for four days. The SiO₂-TiO₂ sol-gel is then spin coated at approximately

800 rpm onto a fused silica substrate. The coated substrate is then placed in a preheated furnace at 400 °C for 30 min. SiO₂-TiO₂ thin films with different stoichiometries, approximately 500 nm thick, have been prepared for the THG measurement performed here. Such thicknesses had to be reached in order to be able to observe a change in the Maker fringes when the film was deposited. The optical quality of the films is greatly improved by using more dilute solutions deposited at higher speeds than those used in our experiments. Thinner single-mode waveguides using a similar process have been deposited at the University of Arizona showing waveguide losses less than 1.5 dB/cm at 0.5145 μ m for 50% TiO₂ content. However, the waveguide loss dependence on TiO₂ concentration has not been investigated. We also investigated films made from a commercial Emulsitone solution believed to be 50:50 mole% from refractive index measurements. The refractive index measurements also indicate that the deposited sol-gel films are fully dense, as shown in Table I.¹⁰

THG is an ideal technique for the measurements of relatively small values of $\chi^{(3)}$. The samples considered here consist of a thin film deposited on a much thicker substrate, with a nonlinearity of only up to 20 times that of the substrate. The expected film signal is too small to be measured by techniques such as degenerate four wave mixing, or Kerr rotation for directions normal to the film surface. Waveguide versions of these techniques are too tedious for characterizing many samples. To optimally use THG it is desirable to have the product of the film thickness and nonlinearity be comparable to the product of the THG coherence length of the substrate and the substrate nonlinearity. Since the THG coherence length of fused silica at 1.579 μ m is approximately 15 μ m, the third-harmonic electric fields from the film and the substrate are comparable for 1- μ m-thick films. Therefore both the magnitude and the phase of $\chi^{(3)}$ can be measured from the shift and offset of the THG Maker fringes, an example of which is shown in Fig. 1.

THG Maker fringes were obtained by focusing approximately 100 μ J of infrared radiation with a 20 cm focal length lens onto a sample placed in a 200 mTorr vacuum chamber. The sample was rotated by a computer-controlled stepper motor. The THG signal generated was

^{a)}Permanent address: Raytheon Research Division, 131 Spring Street, Lexington, MA 02173.

^{b)}Permanent address: Corporate Research Laboratories /3 M, Building 201-2N-19, 3M Center, St Paul, MN 55144-1000.

^{c)}Permanent address: Center for Laser Research, Oklahoma State University, Stillwater, OK 74078-0533.

^{d)}Permanent address: CREOL, University of Central Florida, 12424 Research Parkway, Orlando, FL 32826.

TABLE 1. We report both the calculated refractive indices and measured ones for some of the samples investigated. The calculated refractive indices were obtained following the formalism of Morey, see Ref. 14. We measured the refractive indices and sample thickness by ellipsometry at 6328 Å.

% TiO ₂	Calculated refractive index at 5893 Å	Measured refractive index at 6328 Å (film thickness)
30	1.6237	1.624 ± 0.001 [610 nm]
50	1.7186	1.734 ± 0.005 [285 nm]
70	1.8157	1.846 ± 0.02 [440 nm]

filtered with a spectrometer and appropriate color filters, and then detected with a photomultiplier. The 1.064, 0.953, and 1.579 μm excitation wavelengths were obtained respectively from an injection-seeded GCR-4 (Quanta Ray) Nd:YAG laser with 8 ns pulses, and the second and third Stokes lines generated by focussing 150 mJ of the second harmonic of the 1.064 μm Nd:YAG line into a hydrogen Raman shifter. Prior to the measurements, a circle of approximately 2 mm in diameter was scribed with a diamond pen onto one of the substrate surfaces. Maker fringes were then taken at this same location for both the bare and coated substrate. This allowed us to obtain both the magnitude and phase of the film's $\chi^{(3)}(3\omega)$ relative to that of each fused silica substrate. The Maker fringe THG technique used here has been described elsewhere.¹¹ Multiple reflections as well as the absorption at 3ω were taken into account in the analysis.

In Fig. 2 we show the wavelength dispersion of $\chi^{(3)}(3\omega)$ obtained from our SiO₂-TiO₂ thin-film samples. A resonant enhancement occurs when the third-harmonic frequency approaches in wavelength the absorption band due to the Ti—O bond. In addition, the phase of $\chi^{(3)}$ varies from 0° to 180°. This phase change, we postulate, is due to

FIG. 1. THG Maker fringes at 1.579 μm of a 50:50 mole % SiO₂-TiO₂ 500-nm thick sol-gel thin film. The dark dots are the experimental data points. The solid line is the best fit to the Maker fringe. The dashed-line represents the THG-Maker fringes of the clean substrate.

FIG. 2. Both the magnitude and phases of $\chi^{(3)}(3\omega)$ are plotted as a function of the third-harmonic wavelength. The absorbance of the 500-nm-thick, 50:50 SiO₂-TiO₂ film is also plotted. The absorbance at 317 nm is 0.60, at 355 nm is 0.15, at 526 nm is 0.01. The error bars were obtained by fitting both sides of the Maker fringes independently and by varying the thickness of the sol-gel film within the error bar of the thickness measurement in the fitting procedure. In addition two sol-gel samples of the same stoichiometric composition were measured.

the presence of the resonance at 3ω , and not due to any neighboring two-photon resonance. The rapid change in the phase of $\chi^{(3)}$ from 90° to 180° between 1.064 and 0.953 μm was observed in all samples. It can be modeled by a homogeneously broadened single oscillator model with a very narrow linewidth for the single-photon transition. This model is only realistic in the nonresonant regime and has been used successfully in interpreting the nonlinearity of glasses and transparent crystals.^{12,13} The error bar for the phase of $\chi^{(3)}(3\omega)$ at 1.579 μm is due to the limited number of fringes recorded at the wavelength as shown in Fig. 1. In order to obtain a good estimate of the phase, two identical samples were measured and both sides of the Maker fringes were fitted. A phase close to 0° is expected because of the lack of any resonance.

In Fig. 3 we show the variation in $|\chi_f^{(3)}/\chi_s^{(3)}|$ as a function of the mole% of TiO₂. In that figure we have plotted the calculated $\chi^{(3)}$ relative to fused silica using the empirical formula derived by Boling *et al.*¹²

$$\frac{\chi_f^{(3)}}{\chi_s^{(3)}} = \frac{K \times 10^{-13}}{\chi_{\text{SiO}_2}} \times \frac{n_d(n_d - 1)(n_d^2 + 2)^2}{12\pi v_d [1.52 + (n_d^2 + 2)(n_d + 1)(v_d/6n_d)]^{1/2}}, \quad (1)$$

where n_d is the linear refractive index at 587 nm and v_d is the Abbe number. It is assumed in Boling's formula that the second-order hyperpolarizability is proportional to the square of the linear polarizability. The resulting propor-

FIG. 3. Relative magnitude of $\chi^{(3)}(3\omega)$ at $1.579 \mu\text{m}$ is plotted vs SiO_2 concentration. The dark triangle represents the measured value of a commercially available solution (EMULSITONE). The error bars were obtained by fitting both sides of the Maker fringes independently and varying the thickness of the sol-gel film within the error bar of the thickness measurement. In addition two sol-gel samples of the same stoichiometric composition were measured.

tionality factor K is determined experimentally. We have estimated the values of the refractive index and the Abbe number by using a fully annealed glass model.¹⁴ By varying the value of K from 70 to 100, we obtained reasonable agreement with the Boling formula, assuming a value of $\chi_{\text{SiO}_2}^{(3)}$ of 3.3×10^{-15} esu.¹³ The value of $K = 70$ agrees with the best fit to the nonlinear interferometry and three-wave mixing (TWM) data on transparent glasses.^{12,13}

In conclusion, we have shown that the THG Maker

fringe technique is ideal for measuring the nonlinear susceptibility of sol-gel glass-like thin films which can be used as nonlinear waveguides. In particular, we have found nonlinearities in SiO_2 - TiO_2 films up to 20 times that of fused silica, one of the largest values measured to date in thin-film glass waveguides.¹⁵

The authors would like to thank Dr. K. DeLong for suggesting this research. We would also like to acknowledge interesting discussions with Professor J. Simmons and Dr. V. Mizrahi. W. E. Torruellas's research has been supported by a grant from Eastman-Kodak. This research was supported by NSF (EET-8814663).

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