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MEASUREMENT OF THE THIRD ORDER SUSCEPTIBILITY OF ORIENTED TRANS-POLYACETYLENE

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ABSTRACT

We report on the measurement of the electronic $\chi^{(3)}$ of trans-polyacetylene by optical third harmonic generation. The obtained value at 1.064 µm is $\chi^{(3)}(3\omega) = (8.1 \pm 4) \times 10^{-9}$ esu, which is an order of magnitude larger than that of non-oriented samples.

INTRODUCTION

In this paper, we report on optical third harmonic generation in thin film samples of trans-polyacetylene. The measurements were performed at the wavelength of the Nd:YAG laser, λ = 1.064 µm.

The samples having thicknesses of ∿0.3 µm were prepared on fused silica substrates by an improved technique resulting in fully oriented crystalline trans-polyacetylene material [1]. The thin films show a homogeneous and compact morphology and high-quality surfaces. These properties allowed the reliable determination of the linear anisotropic optical constants by polarized reflectivity measurements [2]. In posession of accurate values of the linear optical data, the third order nonlinearity can be extracted from optical third harmonic generation (THG) experiments.

THG in polyacetylene shows some peculiar features not present in insulating optical crystals. In fact, the very large refractive index of the material leads to a reflected fundamental wave inside

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the plane-parallel slab medium which has an amplitude comparable to that of the forward propagating fundamental field. As a result, there are four harmonic waves with different wave vectors originating from the mixing of the forward and backward propagating fundamental waves by the third order nonlinear polarization [3]. The reflected and transmitted output harmonic fields originate from the interference of the waves mentioned before. Taking $n(\omega) = 4.06$, $\alpha(\omega) = 2.60\mathrm{x}10^4\ \mathrm{cm}^{-1}$; $n(3\omega) = 0.513$ and $\alpha(3\omega) = 4.28\mathrm{x}10^5\ \mathrm{cm}^{-1}$ for trans-$(CH)_x$ for light polarized parallel to the chain direction, we can derive the transmitted third harmonic intensity as a function of the sample thickness as shown in Fig. 1. The fringes clearly reflect the interference of the generated harmonic waves inside the nonlinear film. As it can be seen from Fig. 1, neglecting this interference may lead to large errors in the evaluation of the THG measurement for sample thicknesses less than the absorption length at the fundamental wavelength ($l < 1/\alpha(\omega)$, in our case $1/\alpha(\omega) \approx 0.4\mu\mathrm{m}$)

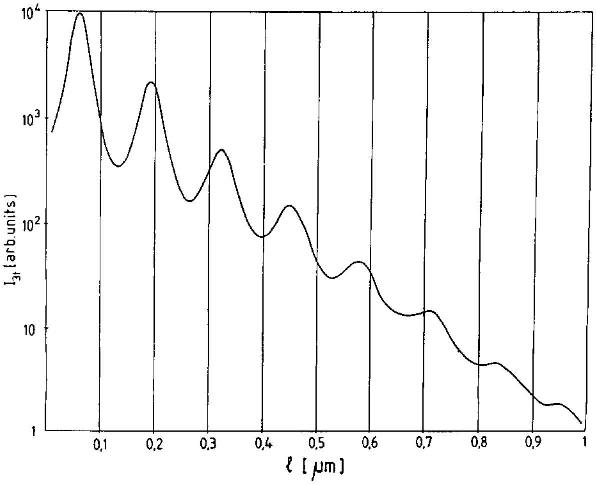

Fig. 1. Calculated intensity of the transmitted third-harmonic signal as a function of sample thickness l showing interference effects.

EXPERIMENTAL RESULTS

The light source in our measurements was a Q-switched Nd:YAG laser delivering 10 ns optical pulses at $\lambda = 1.064\ \mu\mathrm{m}$ at a repetition rate of 10 pulses per second. The beam was split into a reference beam and a pump beam. The reference beam passed through a silica plate to provide a reference third harmonic signal for normalization against laser fluctuations. The sample beam acted as the fundamental beam for THG either in the thin film sample or in another silica plate used for calibration of the third harmonic signal originating from the trans-$(CH)_x$ material. The third harmonic output from the calibration silica plate having a thickness of 0.2 mm is shown in Fig.2 as a function of the angle of incidence ϑ of the fundamental beam polarized perpendicular to the plane of incidence. The influence of the surrounding air on the THG experiment [4] was considerably eliminated by tight focusing of the fundamental beam [5].

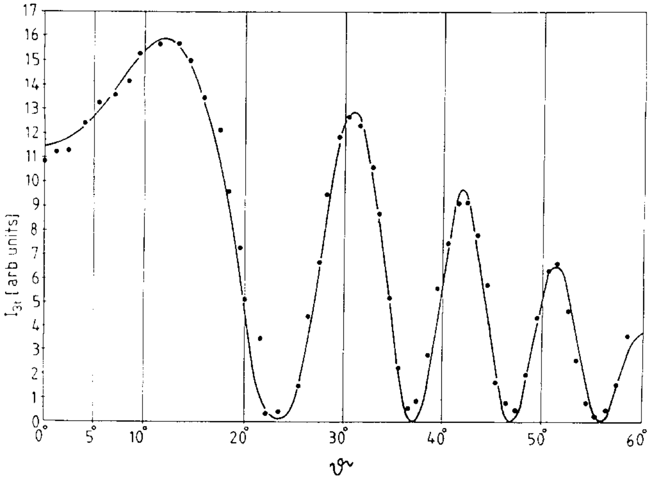

Fig. 2. Maker fringes of the reference third harmonic signal from a silica plate.

The absolute calibration of $\chi^{(3)}$ of trans-$(CH)_x$ was performed by comparing the signal from the semiconductor film with that from the calibration silica plate. Using the formulas derived in Ref. [6]

$$|\chi^{(3)}_{xxxx}(\omega,\omega,\omega)|_{(CH)_x} \Big/ |\chi^{(3)}(\omega,\omega,\omega)|_{SiO_2} = 2.9 \times 10^{5}$$

Neglecting dispersion, $\chi^{(3)} = 2.8\times10^{-14}$ esu for silica as determined by Meredith et al.[6] at $\lambda = 1.907$ µm. Using this value, we obtain for oriented crystalline trans-polyacetylene:

$$\chi^{(3)}_{xxxx}(\omega,\omega,\omega) = (8.1 \pm 4) \times 10^{-9} \text{ esu} \quad \text{for } \lambda = 1.064 \ \mu\text{m}$$

This value is more than an order of magnitude larger than the $\chi^{(3)}$ of non-oriented Shirakawa-type trans-polyacetylene [8],[9].

The strong enhancement of the third order nonlinear susceptibility is mainly due to the orientation of the $(CH)_x$ chains and the high density of the material. This exceptionally high value of the electronic $\chi^{(3)}$ implies a large nonlinear index of refraction $n_2 = 7 \times 10^{-3}$ GW^{-1} cm^2 where n_2 is defined by $\Delta n = n_2 I$ (Δn is the change of the refractive index caused by strong light intensity I). For comparison, the nonlinear index of CS_2: $n_2 = 3 \times 10^{-5}$ GW^{-1} cm^2. Taking into account the fact that trans-polyacetylene is transparent in the near infrared ($E_g = 1.5$ eV), the large value of n_2 combined with a high damage threshold and a fast response time makes this material attractive for nonlinear optical applications in the picosecond and femtosecond regime.

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