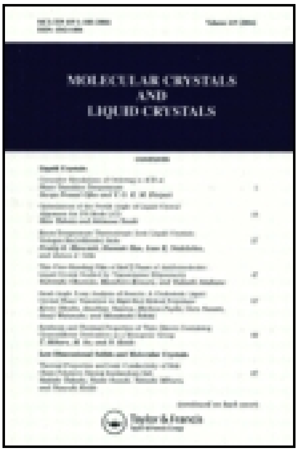

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Masafumi Yamashita [a], Atsuhiko Wajiki [a], Akihiko Mito [b], Chen Lingbing [c], Atsuo Morinaga [a] & Toshiharu Tako [a]
[a] Dept. of Phys, Science University of Tokyo, Noda, 278, Japan
[b] N. R. N. Lab. of Metrology, Umezono 1, Tsukuba, 305, Japan
[c] Dept. of Phys, Fudan University, Shanghai, P. R. China

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# ANISOTROPY OF $\chi^{(3)}$ OF TIN-PHTHALOCYANINE DEPOSITION FILM

MASAFUMI YAMASHITA, ATSUHIKO WAJIKI, *AKIHIKO MITO,
**CHEN LINGBING, ATSUO MORINAGA AND TOSHIHARU TAKO
Dept.of Phys. Science University of Tokyo, Noda 278, Japan
*N.R.N.Lab.of Metrology, Umezono 1, Tsukuba 305, Japan
**Dept.of Phys. Fudan University, Shanghai, P.R.China

Abstract Third-order electric susceptibility $\chi^{(3)}$ of tin-phthalocyanine film deposited on a boro-silicated glass plate coated with rubbing-treated polyimide thin film was measured by a method of THG Maker-fringe technique. In the resonant absorption spectral range, the maximum values of $\chi^{(3)}$ of aggregated tin-phthalocyanine were $220\times10^{-12}$esu obtained in the direction perpendicular to the rubbing direction, but the values parallel to the rubbing were $47\times10^{-12}$esu. The large anisotropy of $\chi^{(3)}$ was induced by a preferred orientation of tin-phthalocyanine microcrystals when anisotropic substrates were heated at 200°C.

## INTRODUCTION

Many kinds of phthalocyanine compounds have been synthesized and studied because of great interests in electric and optical applications as photoconductors and photosensitive devices. In particular, studies of nonlinear optical properties of metal-phthalocyanine (M-Pc) derivatives have developed rapidly. There have been second-harmonic generation (SHG) and third-harmonic generation (THG) studies on some M-Pc's[1], but it has been difficult for studies on tin-phthalocyanine (SnPc) to be found. Optical third-order electric susceptibility $\chi^{(3)}$ of SnPc aggregates deposited on a quartz glass plate was examined by a method of THG Maker-fringe technique. The values of $\chi^{(3)}$ obtained were $30 \sim 50\times10^{-12}$esu[2] and these were almost the same order as those of VOPC or TiOPc.

The purpose of this study is to examine absorption spectra and $\chi^{(3)}$ of SnPc aggregates deposited on a boro-silicated glass plate coated with rubbing-treated polyimide thin film, i.e., a treated substrate.

## EXPERIMENTAL AND DISCUSSIONS

Tin-phthalocyanine (SnPc) material repurified was deposited on the treated substrates at $10^{-4}$Pa. The evaporation rate was regulated at 0.1nm/s. The thickness of SnPc film deposited was 40 to 300nm, which was monitored by a quartz crystal oscillator (ULVAC CRTM-5000). The substrates were kept at room temperature or heated at 200°C , since the deposited molecules would easily diffuse on the heated substrates and be oriented with minimum free energy. Then, it could be expected that the aggregated layers would be built up to a preferred orientation.

The quality of SnPc aggregates was evaluated by a measurement of optical absorption with using a double beam spectrometer (Shimadzu UV -3000). For the absorption measurements, two identical polarizers were added into the optical paths. Figure 1 shows the polarized absorption spectra of SnPc deposited on the substrates heated at 200°C. As is obvious from the figure, the absorption peak about 790nm, called Q band, separates into two peaks. One peak appears at about 760nm for **E**⊥b and the other at about 815nm for **E**∥b, respectively, where b is the rubbing direction and **E** the direction of linear polarized incident light. It is assumed that the explicit separation of spectral peaks between different polarization direc-

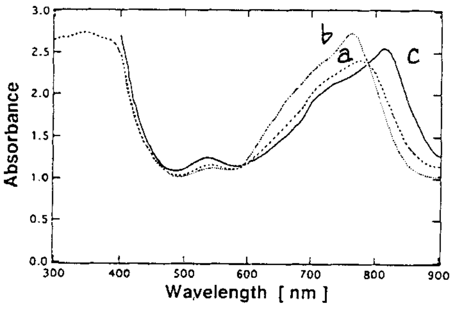

FIGURE 1 Absorption spectra of SnPc aggregates on substrates heated at 200°C.
a : normal spectra of Q band,
b,c : polarized spectra for **E**⊥b and **E**∥b.

tions of incident light is affected by a molecular stacking structure. The optical absorption in Q band of SnPc is caused by the $\pi$-$\pi^*$ transitions, and the dichroism of SnPc deposition film shown on the heated substrates depends on the degenerates of excited energy states and the distribution of electron densities in SnPc with non-planar molecular structure.

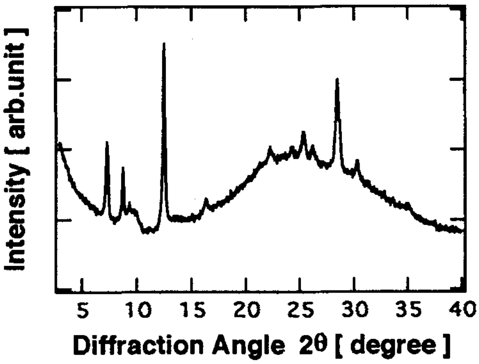

FIGURE 2 X-ray diffraction pattern of SnPc on heated substrates.

Figure 2 shows the angular positions of X-ray diffraction lines from the heated substrates. The crystal structure was estimated to be the triclinic system.[3,4] It seems that the large majority of the aggregates have a preferential orientation and the regularity of molecular stacking in the crystal system increases. These are closely related with an increase in $\chi^{(3)}$.

Optical third-harmonic generation (THG) of SnPc deposition film was measured by a method of THG Maker-fringe technique. Both a vertically polarized Q-swiched Nd:YAG laser at wavelength 1.064μm and a dye-laser were used together. Three fundamental wavelengths 1.89μm, 2.10μm and 2.19μm were used, respectively, to measure the TH intensities dependent on two different polarization directions shown in Figure 1.

Figure 3 shows TH intensities measured with turning the film around the axis parallel to the film surface. The fundamental wavelength as an input beam was 2.10μm and TH wavelength was 700nm. The TH intensities express in values relative to a standard crystal, i.e., a quartz plate ($\chi^{(3)}=1\times10^{-14}$esu). It was found that the intensities

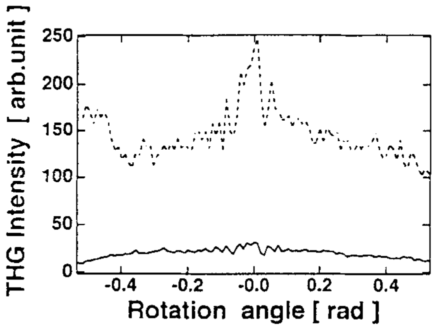

FIGURE 3 THG Maker-fringes for SnPc film at 700nm.
dashed line : for **E**⊥b,
solid line : for **E**∥b.

for **E**⊥b increased dramatically comparing with those for **E**∥b.

The relation between TH intensity $J_{3\omega,s}$ and third-order susceptibility $\chi^{(3)}$ for the examined film is generally given as follows :

$$|\chi_s^{(3)}| = \frac{2}{\pi}\sqrt{\frac{J_{3\omega,s}}{J_{3\omega,r}}\frac{1}{f_s}}\frac{l_r}{l_s}|\chi_r^{(3)}| ,$$

where

$$l_r = \frac{\lambda}{6\Delta n}$$

$$f_s = \frac{4\{1-\exp(-\alpha_{3\omega}l_s/2)\}}{\alpha_{3\omega}{}^2 l_s{}^2}$$

and $l_r$ is the coherence length, $l_s$ is the film thickness, the subscripts r and s represent the reference crystal and the film, respectively, $\lambda$ is the wavelength of the fundamental wave, $\alpha_{3\omega}$ is the absorption coefficient and $\Delta n$ is the difference in refractive indices between the fundamental and TH waves. Following the above procedure, $\chi^{(3)}$ was calculated.

The relation between the values of $\chi^{(3)}$ obtained in this study and TH wave is listed and in Table 1 and shown in Figure 4. As is obvious from the table and figure, the high anisotropy of susceptibility

TABLE 1 Values of $\chi^{(3)}$ of SnPc deposition film at three fundamental wavelengths. ($\chi^{(3)}\times10^{-12}$esu)

| | fundamental wave | | |
|---|---|---|---|
| | 1.89μm | 2.10μm | 2.19μm |
| **E**∥b<br>room temp. | 17 | 58 | 69 |
| **E**⊥b<br>room temp. | 19 | 61 | 68 |
| **E**∥b<br>200°C | 30 | 43 | 47 |
| **E**⊥b<br>200°C | 84 | 180 | 220 |

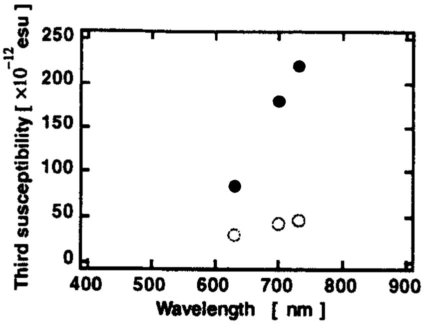

FIGURE 4 Relation between $\chi^{(3)}$ and TH wave.
● : for **E**⊥b, ○ : for **E**∥b.

depends on TH wave and polarization directions of absorption spectra. Values of $\chi^{(3)}$ and absorbance for **E**⊥b were constantly higher than those for **E**∥b with using the heated substrates. And, the resonant enhancement in $\chi^{(3)}$ was obtained by comparing with the absorption spectra. It seems that these results will depend on the overlapping of conjugated π system in a molecular stacking structure, i.e., the preferential direction of microcrystallites. It has been known that the susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ is enhanced when the triple of incident photon energy approches to the energy gap.[5] Then, a model of three-photon resonance holds in SnPc aggregates.

In conclusion, TH intensities of SnPc deposition film were measured and the large values of third-order optical susceptibility $\chi^{(3)}$ were obtained. The maximum value was $220\times10^{-12}$esu for $\mathbf{E}\perp b$ on the heated substrates. It was larger than other metal-phthalocyanines.[6] The high anisotropy of susceptibility shows the same direction as that of absorption spectra. The result suggests that the conjugated π-system overlaps in a preferential direction caused by the treated and heated substrates. Further insight into the orientation of SnPc aggregates and temperature dependence have been in progress.

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