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## Third-Order Nonlinear Optical Properties of Sol-Gel Derived FeTiO<sub>3</sub> Thin Films

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Third-order nonlinear optical properties of sol-gel derived FeTiO<sub>3</sub> thin films have been investigated by the third-harmonic generation (THG) method, and the effect of valence of Fe ions on the third-order nonlinear optical susceptibility,  $\chi^{(3)}$ , has been examined. The  $\chi^{(3)}$  value of FeTiO<sub>3</sub> thin film was  $3.3 \times 10^{-12}$  esu, which is comparable to those for TiO<sub>2</sub> polymorphs (rutile and anatase) but one order of magnitude lower than that of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Second-hyperpolarizability per Fe<sup>2+</sup>O formula unit,  $\gamma(\text{Fe}^{2+}\text{O})$ , was one fourth to one third of  $\gamma(\text{Fe}_{2/3}^{3+}\text{O})$  and about four times as large as  $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$ , indicating that the  $\chi^{(3)}$  value of FeTiO<sub>3</sub> may be dominated by the  $\gamma(\text{Fe}^{2+}\text{O})$  rather than  $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$ .

KEY WORDS: FeTiO<sub>3</sub>/  $\chi^{(3)}$ / Second-hyperpolarizability/ Sol-gel method

### 1. INTRODUCTION

As previously reported,<sup>1)</sup> the third-order nonlinear optical susceptibility,  $\chi^{(3)}$ , of the sol-gel derived  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin film was  $5.8 \times 10^{-11}$  esu, which is about 600 times as high as that of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single crystal with the same corundum structure. This was ascribed to the much higher refractive index of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> than that of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> on the basis of Miller's rule<sup>2,3)</sup> which predicts that a material with high refractive index shows a high  $\chi^{(3)}$ . Since Fe element which is a transition metal having *d* electrons may be responsible for the high  $\chi^{(3)}$ ,<sup>1)</sup> the effect of valence or *d* electronic structure of Fe ions on the third-order nonlinear optical properties is also of great interest. FeTiO<sub>3</sub> (ilmenite) was selected as a Fe<sup>2+</sup>-containing compound, in which both Fe<sup>2+</sup> and Ti<sup>4+</sup> ions are substituted for Al<sup>3+</sup> ions in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. In addition, it should be noted here that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub><sup>1)</sup> and TiO<sub>2</sub><sup>4)</sup> with high refractive index more than 2.5 are known to exhibit very high  $\chi^{(3)}$  of  $10^{-12}$  to  $10^{-11}$  esu.

In the present study, FeTiO<sub>3</sub> thin films have been prepared on the SiO<sub>2</sub> glass substrates by the sol-gel method. Third-order nonlinear optical properties of the FeTiO<sub>3</sub> thin films have been investigated by the third-harmonic generation (THG) method and the effect of valence of Fe ions on the third-order nonlinear optical susceptibility has been examined.

### 2. EXPERIMENTAL

#### 2.1 Preparation of FeTiO<sub>3</sub> thin films

FeTiO<sub>3</sub> thin films were prepared by the sol-gel method. As starting solution,

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Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O–Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>–CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH–CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub> solutions were selected. The chemical composition of the solution was 1 : 1 : 40 : 4 in molar ratio. Iron (III) nitrate enneahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) was first dissolved in a solution of 2,4-pentanedione (CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>) and half of a prescribed amount of 2-methoxyethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH). Then, titanium isopropoxide (Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) which was diluted by the remainder of CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH in advance was mixed with the solution. Coating solutions were allowed to stand at 60°C for 24 h prior to use.

Dip-coating was used for film formation. A SiO<sub>2</sub> glass substrate was immersed in a coating solution, and pulled up at a rate of 3 cm min<sup>-1</sup>. The film was heated at 800°C for 10 min immediately after each coating procedure. This cycle was repeated 10 times to attain the desired film thickness of about 0.3 μm. To enhance the laser-induced damage threshold (LIDT),<sup>5)</sup> a SiO<sub>2</sub> coating was further applied onto the FeTiO<sub>3</sub> film. Otherwise, a part of FeTiO<sub>3</sub> film peeled off upon laser irradiation. In the present coating process, films are formed on both surfaces of the SiO<sub>2</sub> glass substrate. The FeTiO<sub>3</sub> and additional SiO<sub>2</sub> films on one surface were removed to minimize the interference effect<sup>6)</sup> of THG light in the THG measurement.

## 2.2 Characterization of FeTiO<sub>3</sub> thin films

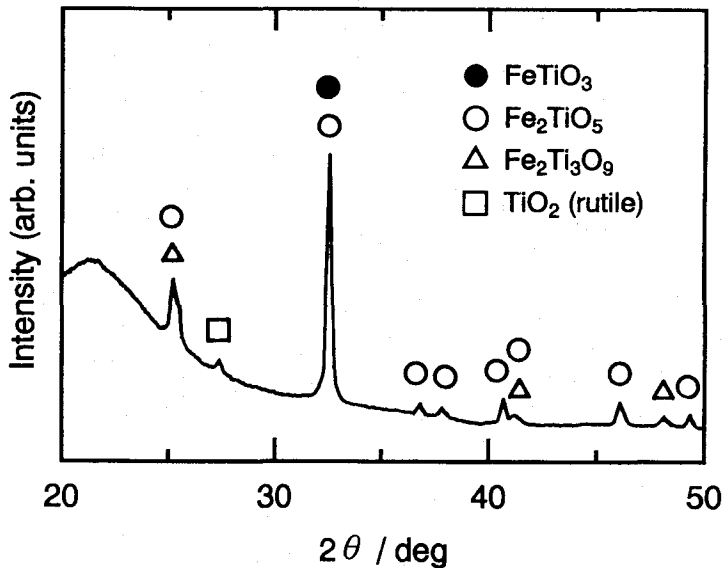
The crystalline phases precipitated in the FeTiO<sub>3</sub> thin film were identified by X-ray diffraction method using CuKα radiation. The refractive index of FeTiO<sub>3</sub> film was determined by an ellipsometer in the wavelength region from 500 to 1,000 nm. The ellipsometry measurement also gave the film thickness. The absorption spectra of FeTiO<sub>3</sub> films with and without additional SiO<sub>2</sub> coating were measured in the wavelength region from 200 to 2,000 nm by a UV-visible spectrophotometer.

THG measurement of FeTiO<sub>3</sub> thin film was made by means of a nonlinear optical measurement apparatus (Tokyo Instruments, Inc., Tokyo, Japan). The Q-switched Nd:YAG laser was operated at the fundamental wavelength of 1,064 nm with a pump pulse duration of 10 ns and a peak power density of 200 MW cm<sup>-2</sup>. The laser frequency at 1,900 nm was obtained directly by stimulated Raman scattering in a high pressure hydrogen cell, which was excited by the Nd:YAG line at 1,064 nm. The THG light at 633 nm, which was isolated by a monochromator, was detected by a photomultiplier connected to a box-car integrator. The sample was mounted on a goniometer and rotated at 0.25° intervals from -40 to +40° by a computer-controlled stepper motor with respect to the axis perpendicular to the incident light.

In both absorption spectrum and THG measurements, the samples were irradiated from the side without films.

## 3. RESULTS

Figure 1 shows X-ray diffraction pattern of FeTiO<sub>3</sub> thin film. The main crystalline phase was FeTiO<sub>3</sub> (ilmenite) although small amounts of Fe<sub>2</sub>TiO<sub>5</sub> (pseudobrookite), Fe<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub> (pseudorutile) and TiO<sub>2</sub> (rutile) phases were precipitated. In the present study, Ti-containing solution was mixed with Fe-containing solution. The reversed mixing lead to the increased TiO<sub>2</sub> phase. The reducing treatment of the resultant film was attempted in order to convert the residual Fe<sup>3+</sup> to Fe<sup>2+</sup> ions. Although impurity phases such as Fe<sub>2</sub>TiO<sub>5</sub> and Fe<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub> decreased, the film became slightly blackish in color probably due to the formation of the reduced

Fig. 1. X-ray diffraction pattern of FeTiO<sub>3</sub> thin film.

species such as Fe metal or Ti<sup>3+</sup> ion, which could not be detected by an X-ray diffraction. The crystallite size in the FeTiO<sub>3</sub> film was 30 nm.

### 3.1 Refractive index and optical transmittance

The wavelength dependence of refractive index,  $n$ , for FeTiO<sub>3</sub> thin film is shown in Figure 2. It is seen that the refractive index of FeTiO<sub>3</sub> film decreases with increasing wavelength. Figure 3 presents a linear plot of  $(n^2 - 1)^{-1}$  versus  $E^2$  for FeTiO<sub>3</sub> thin film based on Wemple's equation<sup>7)</sup>

$$\frac{1}{n^2 - 1} = \frac{E_0}{E_d} \frac{E^2}{E_0 E_d} \quad (1)$$

where  $E$ ,  $E_0$  and  $E_d$  are the photon energy, the average oscillator energy and dispersion energy in eV unit, respectively.  $E_0$  and  $E_d$  are important optical properties of materials<sup>7)</sup>. The refractive indices of FeTiO<sub>3</sub> film were estimated as  $n_{3\omega} = 2.33$  at 633 nm and  $n_{\omega} = 2.17$  at 1,900 nm, and the coherence length,  $l_c = 1.9/[6(n_{3\omega} - n_{\omega})]$ , was 2.0  $\mu\text{m}$ . The thickness of the FeTiO<sub>3</sub> film obtained by 10 dippings was typically 0.27  $\mu\text{m}$ .

Figure 4 shows the absorption spectra of FeTiO<sub>3</sub> thin films with and without additional SiO<sub>2</sub> coating. Both spectra have a number of mountains and troughs arising from the interference of light. It is seen that the additional SiO<sub>2</sub> coating reduces the optical loss due to reflection especially in the wavelength region above about 400 nm. Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in octahedral coordination are known to show absorption bands around 1,100 and 800 nm, respectively.<sup>8)</sup> The difference in absorbance due to reflection loss between both spectra is relatively small around 1,100 and 800 nm, indicating that the present FeTiO<sub>3</sub> film includes Fe<sup>3+</sup>-containing compounds in accordance with the result of X-ray diffraction measurement. The optical band gap,  $E_g$ , of FeTiO<sub>3</sub> film was estimated to be 2.2 eV.

### 3.2 Evaluation of $\chi^{(3)}$ value

The THG intensities as a function of the rotation angle are given for (a) FeTiO<sub>3</sub> film and (b)

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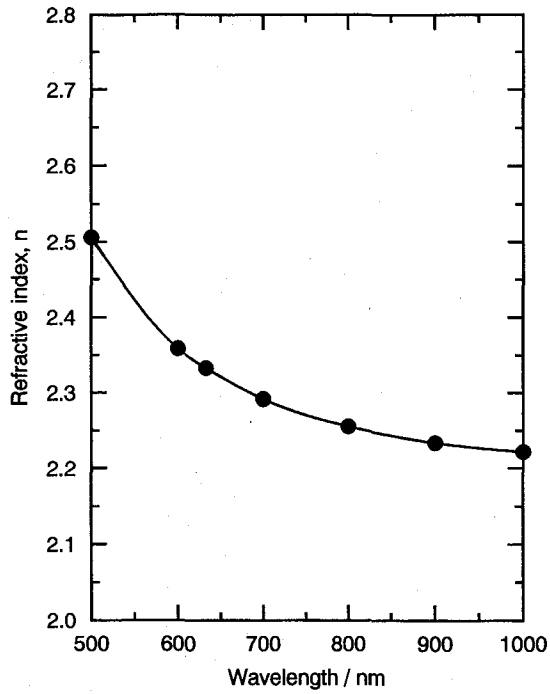


Fig. 2. Wavelength dependence of refractive index,  $n$ , for FeTiO<sub>3</sub> thin film.

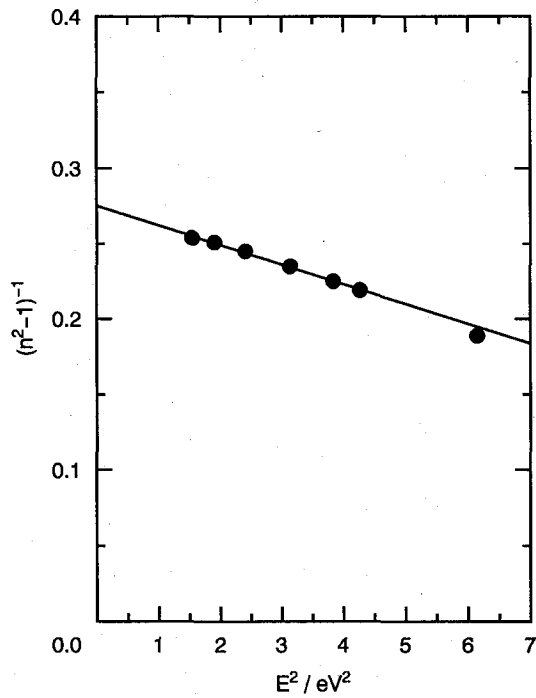


Fig. 3. A Linear plot of  $(n^2 - 1)^{-1}$  versus  $E^2$  for FeTiO<sub>3</sub> thin film.

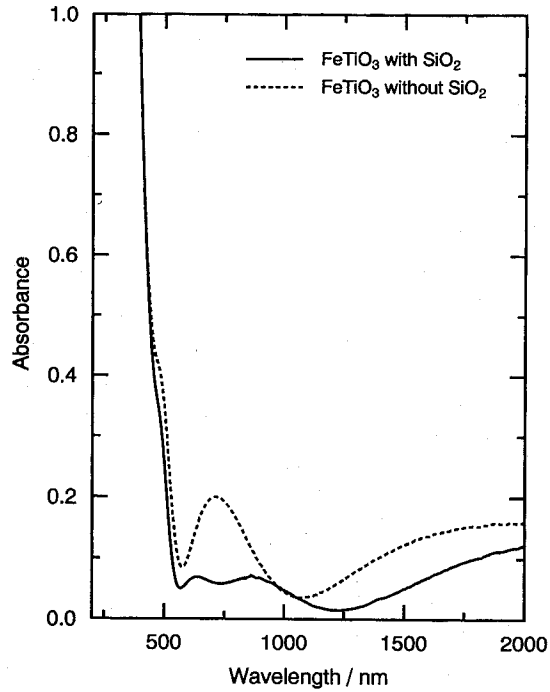


Fig. 4. Absorption spectra of FeTiO<sub>3</sub> thin films with and without additional SiO<sub>2</sub> coating.

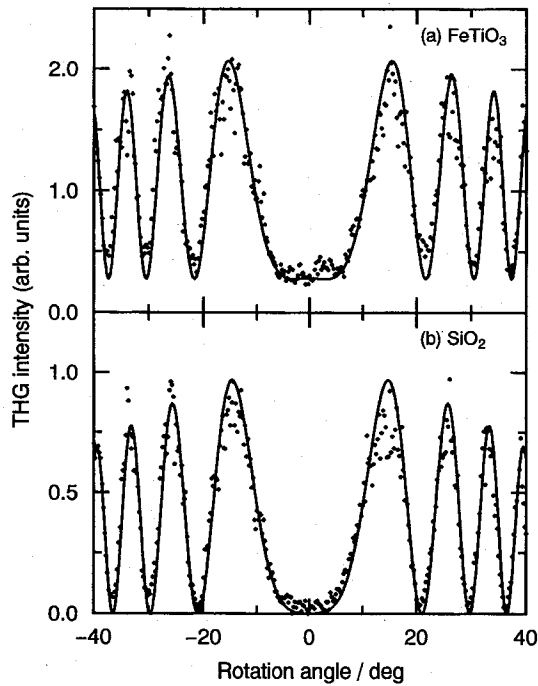


Fig. 5. THG intensities as a function of rotation angle for (a) FeTiO<sub>3</sub> film and (b) SiO<sub>2</sub> glass. Solid line is the best fitted curve for the plotted data.

SiO<sub>2</sub> glass in Figure 5. The THG intensity pattern of FeTiO<sub>3</sub> film clearly shows the interference between the THG lights from FeTiO<sub>3</sub> film and SiO<sub>2</sub> glass substrate as previously reported<sup>6</sup>. The THG intensity was obtained by the least squares method as solid line in Fig. 5.

In the present study,  $\chi^{(3)}$  value was determined by the equation<sup>9</sup>

$$\chi_{\text{film}}^{(3)} = \frac{2}{\pi} \chi_{\text{SiO}_2}^{(3)} \frac{l_{c,\text{SiO}_2}}{l} \sqrt{\frac{I_{3\omega,\text{film}}}{I_{3\omega,\text{SiO}_2}}} \sqrt{\frac{n_{\omega,\text{film}}^3 n_{3\omega,\text{film}} T_{\omega,\text{SiO}_2}^3 T_{3\omega,\text{SiO}_2}}{n_{\omega,\text{SiO}_2}^3 n_{3\omega,\text{SiO}_2} T_{\omega,\text{film}}^3 T_{3\omega,\text{film}}}} \quad (\text{esu}), \quad (2)$$

where  $I$  denotes the THG peak intensity. The film thickness is used for  $l$ , because the film thickness is less than the coherence length. The values of  $\chi_{\text{SiO}_2}^{(3)} = 2.8 \times 10^{-14}$  esu and  $l_{c,\text{SiO}_2} = 18.1 \mu\text{m}$  were used for SiO<sub>2</sub> glass as both standard sample and substrate.<sup>10</sup>

The intensity of THG signals generated from FeTiO<sub>3</sub> film was determined by the equation<sup>6</sup>

$$I_{\text{film}} = \frac{I_{\text{max}} + I_{\text{min}}}{2} - \frac{I_{\text{substrate}}}{2} = \frac{I_{\text{max}} + I_{\text{min}}}{2} - \frac{I_{\text{SiO}_2}}{2}, \quad (3)$$

where  $I_{\text{max}}$  and  $I_{\text{min}}$  are the upper and lower envelopes of the superimposed THG intensity pattern. The contribution of THG light from the additional SiO<sub>2</sub> film on the FeTiO<sub>3</sub> film was neglected, because  $\chi_{\text{SiO}_2}^{(3)}$  is low and the thickness of SiO<sub>2</sub> film (less than about 0.2  $\mu\text{m}$ ) is much smaller than the coherence length. The  $\chi^{(3)}$  value of FeTiO<sub>3</sub> film was determined to be  $3.3 \times 10^{-12}$  esu.

## 4. DISCUSSION

### 4.1 Relationship between $\chi^{(3)}$ and refractive index, $n$

It is possible to estimate  $\chi^{(3)}$  of a material from refractive index,  $n$ , according to Miller's rule<sup>2,3</sup>

$$\chi^{(3)} = [\chi^{(1)}]^4 \times 10^{-10} \quad (\text{esu}), \quad (4\text{-a})$$

and

$$\chi^{(1)} = \frac{n^2 - 1}{4\pi}. \quad (4\text{-b})$$

The  $\chi^{(3)}$  value calculated for FeTiO<sub>3</sub> film from Miller's rule was  $7.6 \times 10^{-13}$  esu, which is lower by a factor of about four than the measured  $\chi^{(3)}$  value of  $3.3 \times 10^{-12}$  esu.

Figure 6 shows a relationship between  $\chi^{(3)}$  and refractive index,  $n_{\omega}$ , at 1,900 nm for FeTiO<sub>3</sub> thin film and other nonlinear optical materials reported so far.<sup>1,4,9-16</sup> It is seen that inorganic materials with high refractive index inherently exhibit high optical nonlinearity.

The  $\chi^{(3)}$  values of organic polymers such as polydiacetylene (PDA)<sup>14</sup> and poly(2,5-dimethoxy *p*-phenylene vinylene) (MO-PPV)<sup>15</sup> deviate from the relation to a considerable extent, due to the enhancement by the so-called three-photon resonance or near three-photon resonance<sup>17</sup>. Since the measured  $\chi^{(3)}$  includes the significant contribution of the imaginary part, there are no simple relations between  $\chi^{(3)}$  and refractive index for these organic materials, that is, Miller's rule does not hold.

### 4.2 Relationship between $\chi^{(3)}$ and optical band gap, $E_g$

One can expect that an enhancement in  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$  occurs when in a material a frequency of interacting light approaches either one of one-, two- or three-photon resonance frequencies according to the relation<sup>17</sup>

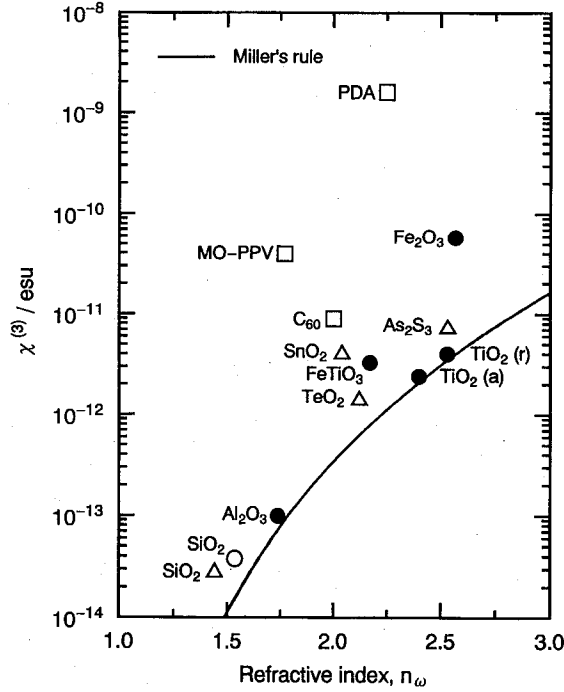


Fig. 6. Relationship between  $\chi^{(3)}$  and refractive index,  $n_\omega$ , at 1,900 nm for FeTiO<sub>3</sub> thin film and other nonlinear optical materials.<sup>1,4,9-16)</sup> Circle, triangle and square denote inorganic crystal, inorganic amorphous material and organic material, respectively. Closed circles are the data measured by the present authors. The letters of *r* and *a* in parentheses denote rutile and anatase, respectively. PDA: polydiacetylene, MO-PPV: poly(2,5-dimethoxy *p*-phenylene vinylene).

$$\chi^{(3)}(-3\omega; \omega, \omega, \omega) \propto \frac{N}{\hbar} \sum_{gnm'n'} \rho(g) F(\omega) \Omega_{gn} \Omega_{nm} \Omega_{mn'} \Omega_{n'g} \text{ (esu)}, \quad (5-a)$$

and

$$F(\omega) = \frac{1}{(E_{ng} - 3\omega)(E_{mg} - 2\omega)(E_{n'g} - \omega)} + \frac{1}{(E_{ng} + \omega)(E_{mg} - 2\omega)(E_{n'g} - \omega)} \\ + \frac{1}{(E_{ng} + \omega)(E_{mg} + 2\omega)(E_{n'g} - \omega)} + \frac{1}{(E_{ng} + \omega)(E_{mg} + 2\omega)(E_{n'g} + 3\omega)}, \quad (5-b)$$

where  $\rho(g)$ ,  $E_{ij}$  and  $\Omega_{ij}$  are the density matrix element of fundamental state, the energy difference between states *i* and *j* in  $\hbar$  ( $=h/2\pi$ ,  $h$ : Planck's constant) unit and the transition matrix elements between states *i* and *j*, respectively. For materials having optical band gap,  $E_g$ , higher than three-photon energy,  $3\omega$ , the three-photon resonance makes the greatest contribution to the enhancement of  $\chi^{(3)}$ . Then, to a good approximation, the most significant term due to the three-photon resonance in Eq. (5) may be expressed as follows:

$$\chi^{(3)} = \frac{A}{(E_g - 1.96)(E_g - 1.31)(E_g - 0.65)} \text{ (esu)} \quad (E_g > 1.96), \quad (6)$$

where *A* is the phenomenological constant.

Figure 7 gives a relationship between  $\chi^{(3)}$  and optical band gap,  $E_g$ , for FeTiO<sub>3</sub> thin film and



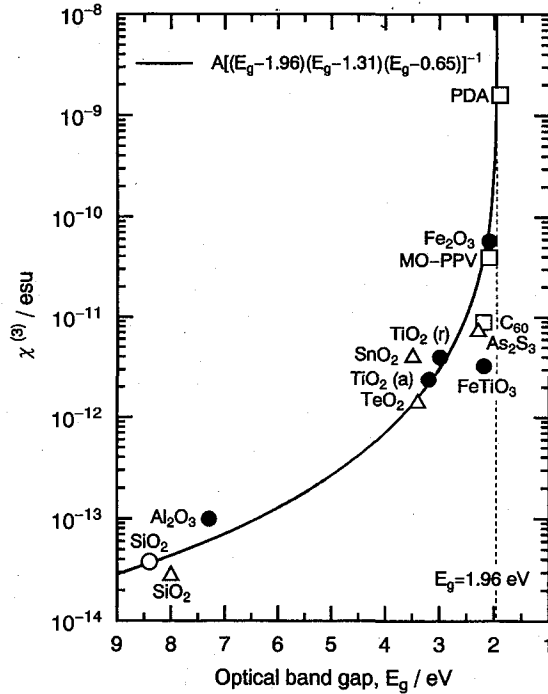


Fig. 7. Relationship between  $\chi^{(3)}$  and optical band gap,  $E_g$ , for FeTiO<sub>3</sub> thin film and other nonlinear optical materials. References and notations are the same as in Fig. 6.

other nonlinear optical materials shown in Fig. 6. In Fig. 7, for organic materials the absorption edge of exciton absorption is used instead of  $E_g$ . In this figure, the  $\chi^{(3)}$  values of these materials show a clear tendency to increase asymptotically as the  $E_g$  approaches 1.96 eV corresponding to the photon energy of THG signal. This change obeys Eq. (6) when the parameter,  $A$ , takes a value of  $1.4 \times 10^{-11}$ . The  $\chi^{(3)}$  value calculated for FeTiO<sub>3</sub> film from Eq. (6) was  $4.2 \times 10^{-11}$  esu, which is higher by a factor of about ten than the measured  $\chi^{(3)}$  value of  $3.3 \times 10^{-12}$  esu.

The above discussion indicates that the large  $\chi^{(3)}$  value of  $3.3 \times 10^{-12}$  esu for FeTiO<sub>3</sub> film, which is comparable to those for TiO<sub>2</sub> polymorphs (rutile and anatase), is explained by the balanced contributions of two opposite effects, the lower refractive index (negative contribution) and the narrower optical band gap (positive contribution) compared with TiO<sub>2</sub> polymorphs. On the other hand, the  $\chi^{(3)}$  value of FeTiO<sub>3</sub> film is one order of magnitude lower than that of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> because of the lower refractive index and the wider optical band gap compared with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

#### 4.3 Calculation of $\chi^{(3)}$ based on Lines' model

Lines introduced a bond-orbital theory dealing with the contribution of empty  $d$  orbital in addition to  $sp$  orbitals to linear and nonlinear optical properties, giving the following equation to estimate  $\chi^{(3)}$ <sup>18,19</sup>:

$$\chi^{(3)} = \frac{25 \times 10^{-13} d^2 (n_\omega^2 - 1) f_L^3 E_S^6}{3\pi [E_S^2 - E^2]^4} \text{ (esu)} \quad (7)$$

where  $d$  denotes the bond length between cation and anion,  $f_L = (n_\omega^2 + 2)/3$  the Lorentz local-field

correction factor,  $E_S$  the Sellmeier gap which is in practice equal to the average oscillator energy,  $E_0$ , in Eq. (1). From Eq. (7), one can obtain  $\chi^{(3)}$  value of  $2.4 \times 10^{-12}$  esu for  $\text{FeTiO}_3$  film, which is in reasonable accordance with the measured value of  $3.3 \times 10^{-12}$  esu compared with those calculated by the above two empirical laws. This is possibly because two important optical properties (refractive index and Sellmeier gap) are included in Eq. (7).

Weak absorption bands around 1,100 nm (1.13 eV) and 800 nm (1.55 eV) due to the presence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions, respectively, do not always cause two-photon resonance at 1.31 eV, because the process requires parity opposite to one and three-photon related ones. Also, Kajzar et al.<sup>17)</sup> reported that as for PDA films the effect of two-photon resonance on the third-order nonlinear optical susceptibility is smaller than that of three-photon resonance.

#### 4.4 Effect of valence of Fe ion on third-order nonlinear optical properties

In order to make the effect of valence of Fe ions on the third-order nonlinear optical properties clear, microscopic second-hyperpolarizability,  $\gamma$ , is taken into account, because macroscopic  $\chi^{(3)}$  depends on both  $\gamma_i$  and the number density,  $N_i$  of the  $i$ th constituents as follows<sup>20,21)</sup>:

$$\chi^{(3)} = \frac{fL^4}{24} \sum_i N_i \gamma_i \text{ (esu)}, \quad (8)$$

For a metal oxide,  $\text{M}_x\text{O}_y$ ,  $\gamma$  per  $\text{M}_{x/y}\text{O}$  formula unit,  $\gamma(\text{M}_{x/y}\text{O})$ , can be derived as follows:

$$\gamma(\text{M}_{x/y}\text{O}) = \frac{1944 \chi^{(3)} M_w}{N_A (n_w^2 + 2)^4 y D} \text{ (esu cm}^3\text{)} \quad (9)$$

where  $M_w$ ,  $D$  and  $N_A$  are the molecular weight and density of  $\text{M}_x\text{O}_y$  and Avogadro's number, respectively.

Table 1. Microscopic and macroscopic nonlinear optical properties of  $\text{FeTiO}_3$  thin film and other nonlinear optical materials.

	$\gamma(\text{M}_{x/y}\text{O})/\text{esu cm}^3$	$\chi^{(3)}/\text{esu}$	$N_i/\text{cm}^{-3}$	$n_w$	$D/\text{g cm}^{-3}$	$M_w/\text{g mol}^{-1}$
$\text{FeTiO}_3$	$4.8 \times 10^{-35}$	$3.3 \times 10^{-12}$	$6.5 \times 10^{22}$	2.17	5.50	151.73
$\text{FeO}^*$	$9.8 \times 10^{-35}$	—	—	—	—	71.85
$\alpha\text{-Fe}_2\text{O}_3^{1)}$	$3.5 \times 10^{-34}$	$5.8 \times 10^{-11}$	$5.9 \times 10^{22}$	2.57	5.26	159.70
$\text{TiO}_2$ (rutile) <sup>4)</sup>	$2.5 \times 10^{-35}$	$4.0 \times 10^{-12}$	$6.4 \times 10^{22}$	2.53	4.23	79.88
$\text{TiO}_2$ (anatase) <sup>4)</sup>	$2.2 \times 10^{-35}$	$2.4 \times 10^{-12}$	$5.9 \times 10^{22}$	2.40	3.89	79.88
$\text{SiO}_2$ glass <sup>10)</sup>	$4.5 \times 10^{-36}$	$2.8 \times 10^{-14}$	$4.4 \times 10^{22}$	1.44	2.21	60.09

\*:  $\gamma(\text{FeO}) = 3\gamma(\text{Fe}_{1/3}\text{Ti}_{1/3}\text{O}) - 2\gamma(\text{Ti}_{1/2}\text{O})$ .

The  $\gamma(\text{Fe}^{2+}\text{O})$ ,  $\gamma(\text{Fe}_{2/3}^{3+}\text{O})$  and  $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$  values were calculated using  $\chi^{(3)}$  value of  $\text{FeTiO}_3$  film,  $\alpha\text{-Fe}_2\text{O}_3^{1)}$  and  $\text{TiO}_2^{4)}$  to be  $9.8 \times 10^{-35}$ ,  $3.5 \times 10^{-34}$  and  $2.2\text{--}2.5 \times 10^{-35}$  esu  $\text{cm}^3$ , respectively, as shown in Table 1. The  $\gamma(\text{Fe}^{2+}\text{O})$  was one fourth to one third of  $\gamma(\text{Fe}_{2/3}^{3+}\text{O})$ . This may be ascribed to the smaller  $p$ - $d$  overlapping resulting from the longer bond length of Fe-O. This long distance is due to the larger ionic radius of  $\text{Fe}^{2+}$  ion compared with  $\text{Fe}^{3+}$  ion. In fact, the bond lengths of Fe-O and Ti-O in  $\text{FeTiO}_3$  are 2.09 and 2.03 Å,<sup>22)</sup> respectively, whereas those in  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{TiO}_2$  are 2.03<sup>22)</sup> and 1.95–1.96 Å,<sup>23)</sup> respectively.

Since the Ti-O bond length in  $\text{FeTiO}_3$  was assumed to be the same as that in  $\text{TiO}_2$  on calculation of  $\gamma(\text{Fe}^{2+}\text{O})$  value, the true  $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$  value for  $\text{FeTiO}_3$  should be lower than that in

TiO<sub>2</sub> and then the  $\gamma(\text{Fe}^{2+}\text{O})$  value should be larger than  $9.8 \times 10^{-35}$  esu cm<sup>3</sup>. Therefore, it can be said that the  $\chi^{(3)}$  value of FeTiO<sub>3</sub> may be governed by the  $\gamma(\text{Fe}^{2+}\text{O})$  rather than  $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$ .

### 5. SUMMARY

The third-order nonlinear optical properties of the sol-gel derived FeTiO<sub>3</sub> thin films have been investigated by the THG method and the effect of the valence of Fe ions on the third-order nonlinear optical susceptibility has been examined. The following results were obtained.

(1) The  $\chi^{(3)}$  value of FeTiO<sub>3</sub> thin film was  $3.3 \times 10^{-12}$  esu, which is comparable to those for TiO<sub>2</sub> polymorphs (rutile and anatase) but one order of magnitude lower than that of  $\alpha\text{-Fe}_2\text{O}_3$ . This was semiquantitatively interpreted in terms of the refractive index and optical band gap.

(2) The  $\gamma(\text{Fe}^{2+}\text{O})$ , which is one fourth to one third of  $\gamma(\text{Fe}_{2/3}^{3+}\text{O})$ , may be ascribed to the smaller  $p-d$  overlapping resulting from the longer bond length of Fe-O due to the larger ionic radius of Fe<sup>2+</sup> ion compared with Fe<sup>3+</sup> ion.

(3) The  $\gamma(\text{Fe}^{2+}\text{O})$  was about four times as large as  $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$ , indicating that the  $\chi^{(3)}$  value of FeTiO<sub>3</sub> is governed by the  $\gamma(\text{Fe}^{2+}\text{O})$  rather than  $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$ .

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