

Structure and Nonlinear Optical Properties of BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> Glasses

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BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> ガラスの構造と非線形光学特性

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The third order nonlinear optical susceptibilities  $\chi^{(3)}$  of BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses have been measured by the third harmonic generation (THG) method. Raman spectroscopic investigation revealed that Ti<sup>4+</sup> ions mainly exist as 4-coordinated. It was found that the addition of TiO<sub>2</sub> to BaO-B<sub>2</sub>O<sub>3</sub> glass increases the  $\chi^{(3)}$  as well as the refractive index. The positive effect of the TiO<sub>2</sub> on the  $\chi^{(3)}$  was interpreted in terms of the empty *d*-orbital contribution. The largest  $\chi^{(3)}$  obtained is  $3.0 \times 10^{-13}$  esu for 35BaO·55TiO<sub>2</sub>·10B<sub>2</sub>O<sub>3</sub> glass, which is, however, only 10 times larger than that for SiO<sub>2</sub> glass. Such a small enhancement in  $\chi^{(3)}$  is ascribed to the large fraction of 4-coordinated Ti<sup>4+</sup> ions in BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses. It is concluded that, for TiO<sub>2</sub>-containing glasses, the higher  $\chi^{(3)}$  values are attained when the optical basicity is low and the amount of Ti<sup>4+</sup> ion is large. It was found that the modified Lines' relationship between  $\chi^{(3)}$  and  $(n_o^2 + 2)^3 \cdot (n_o^2 - 1) \cdot E_d/E_o^2$  is adopted for this system.

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**Key-words :** Nonlinear optical properties, Third harmonic generation, Transition metal, Coordination state, Modified Lines' relationship

## 1. Introduction

Recently, nonlinear optical (NLO) processes draw special attention especially from the point of ultra-fast switching for the all optical devices.<sup>1-5</sup> In order to attain the optical switching by using laser light with relatively low intensity, the third order nonlinear susceptibility ( $\chi^{(3)}$ ) should be of the order of more than  $10^{-8}$ – $10^{-9}$  esu. However, the largest  $\chi^{(3)}$  which has been attained among the transparent materials is at most of the order of  $10^{-11}$  esu.<sup>5</sup> As a guide to search NLO materials with a large  $\chi^{(3)}$ , there are some semi-empirical rules which predict the  $\chi^{(3)}$  as a function of the refractive index and/or the optical band gap.<sup>5-8</sup> Hashimoto and Yoko<sup>5</sup> have reported that the transition metal oxides (TMOs) are promising NLO materials due to the large refractive index (>2.5) and the small optical band gap which both result from large overlapping between the empty *d*-orbitals of transition metal and O 2*p* orbitals.

Since TiO<sub>2</sub>-containing glasses are characterized by the low optical loss and the high refractive index,<sup>9</sup> they are considered to be a promising NLO material. In fact, the  $\chi^{(3)}$  values of  $1.5 \times 10^{-12}$  and  $3.1 \times 10^{-12}$  esu for a TiO<sub>2</sub> single crystals, which were measured by nearly degenerate three-wave mixing (TWM) and degenerate four-wave mixing (DFWM) methods, respectively, have been reported.<sup>10</sup> For TiO<sub>2</sub>-containing glass systems, Vogel et al.<sup>2-4,11</sup> found that glasses containing Ti<sup>4+</sup> ions have larger optical nonlinearity than those of other transition metal ions which have vacant *d*-orbitals such as Nb<sup>5+</sup> ions. Among TiO<sub>2</sub>-containing systems, BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses which can be prepared by the conventional quenching method may be characterized by a high TiO<sub>2</sub> content glass up to 55 mol% TiO<sub>2</sub> and therefore can be considered as an interesting NLO glass system.

It is known that Ti<sup>4+</sup> ions are 6-coordinated by oxygens in most oxide crystals except for Ba<sub>2</sub>TiO<sub>4</sub> and Rb<sub>2</sub>TiO<sub>3</sub>, in which Ti<sup>4+</sup> ions are 4-coordinated. In this regard, it is interesting to examine the coordination state of Ti<sup>4+</sup> ions in oxide glasses. The coordination environments of Ti<sup>4+</sup> ions are also interesting from the view point of the optical non-

linearity. In the current study, we first investigated the glass structure using the Raman and <sup>11</sup>B NMR spectroscopic methods and then evaluated the  $\chi^{(3)}$  value by the third harmonic generation (THG) method.

Lines has dealt with the contribution of the vacant *d*-orbitals as well as *sp*-orbitals to the linear and nonlinear optical properties.<sup>12</sup> So far, we have applied his bond orbital theory with minor modification to some glass systems which do not contain ions of vacant *d*-orbital for the optical transition (i. e., *p*-block elements).<sup>13</sup> In the current study, we adopted this modified Lines theory to the vacant *d*-orbitals containing glasses and evaluated the *d*-orbital contribution to  $\chi^{(3)}$ .

## 2. Experimental procedure

Reagent grade Ba(NO<sub>3</sub>)<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> (Nacalai Tesque, Inc., Kyoto, Japan), and TiO<sub>2</sub> (Wako Pure Chem. Inc., Ltd., Osaka, Japan) were used as raw materials. The batch compositions (mol%) of BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses are shown in Table 1. A 15 g batch of well mixed reagents was melted in a platinum crucible with a lid at 1000–1100°C for binary and 1400–1450°C for ternary glasses for 15 min using an electric furnace. For TiO<sub>2</sub>-containing glasses, the batches were melted in a flowing O<sub>2</sub> gas in order to avoid Ti<sup>3+</sup> formation. The glasses were obtained by pouring the melts onto the stainless plate and pressing by another one. The glasses were polished to about 1 mm thick for the measurements of various optical properties.

The measurements of the optical absorption spectra, refractive index, Raman and <sup>11</sup>B NMR spectra, and THG were performed in the same manner as described in detail elsewhere.<sup>6-8</sup>

## 3. Results

3.1 Raman spectra of BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses

The Raman spectra of BaO-B<sub>2</sub>O<sub>3</sub> binary glasses are shown in Fig. 1. The band assignment of BaO-B<sub>2</sub>O<sub>3</sub> binary glasses is listed in Table 2. All the glasses show strong peaks at 750–770 and 500 cm<sup>-1</sup>. For 20BaO·80B<sub>2</sub>O<sub>3</sub> glass,

Table 1. Linear and Nonlinear Optical Properties\* of  $x\text{BaO} \cdot y\text{TiO}_2 \cdot (100-x-y)\text{B}_2\text{O}_3$  Glasses

Composition / mol%	Density / $\text{g} \cdot \text{cm}^{-3}$	$T_{3\omega}$ / %	$T_{\omega}$ / %	$n_{\omega}$	$n_{3\omega}$	$E_g$ / eV	$E_d$ / eV	$E_0$ / eV	$R_M$ / $\text{cm}^3 \cdot \text{mol}^{-1}$	$V_M$ / $\text{cm}^3 \cdot \text{mol}^{-1}$	$I/I_{\text{SiO}_2}$	$I_c$ / $\mu\text{m}$	$\chi^{(3)}$ / $10^{-14}$ esu
<b>y=0</b>													
x=0	1.797	90.8	82.6	1.425	1.440	7.2	6.17	6.42	9.91	38.7	0.61	14.5	2.88
x=20	2.822	91.2	90.7	1.518	1.535	6.40	12.3	9.45	9.28	30.6	1.00	13.5	4.33
x=30	3.360	90.7	87.3	1.556	1.578	6.27	12.2	8.64	9.05	28.2	1.46	14.0	5.38
x=40	3.776	90.5	85.7	1.585	1.607	6.01	13.3	8.83	9.14	27.3	1.75	14.7	5.87
<b>x=35</b>													
y=10	3.762	81.6	79.9	1.615	1.649	3.81	11.5	7.24	9.28	26.6	1.47	11.7	7.73
y=20	3.962	80.7	78.8	1.694	1.740	3.66	12.2	7.69	9.79	25.5	1.67	9.34	11.5
y=30	4.004	84.2	80.1	1.769	1.797	3.62	18.3	8.63	10.6	25.5	1.89	8.04	14.9
y=40	4.232	81.3	82.1	1.871	1.893	3.59	25.7	10.3	11.1	24.3	2.07	6.71	21.3
y=50	4.348	85.0	84.1	1.914	1.953	3.57	21.2	8.02	11.2	23.9	2.16	6.22	23.7
y=55	4.397	79.8	78.3	1.943	1.981	3.56	22.6	8.19	11.5	23.9	2.28	5.47	30.4
<b>x=y</b>													
x=20	3.133	80.2	73.2	1.673	1.713	3.58	12.5	6.99	10.6	28.2	1.43	9.58	10.4
x=25	3.502	80.7	76.3	1.704	1.739	3.58	14.4	7.61	10.3	26.6	1.85	8.58	13.4
x=30	3.855	82.1	79.8	1.745	1.775	3.59	16.8	8.26	10.3	25.4	1.89	7.96	14.9
x=35	4.103	86.9	84.9	1.816	1.845	3.60	20.2	8.82	10.9	25.1	2.26	7.23	18.4
x=40	4.344	80.6	81.0	1.847	1.878	3.65	20.9	8.70	11.0	24.6	2.66	7.03	22.7

\*  $n_{3\omega}$ ,  $n_{\omega}$ : the refractive index at 633nm and 1.9 $\mu\text{m}$ .  $T_{3\omega}$ ,  $T_{\omega}$ : apparent transmittance at 633nm and 1.9 $\mu\text{m}$ .  $E_g$ : average excitation energy.  $E_d$ : electronic oscillator strength.  $I_c$ : coherence length.  $I/I_{\text{SiO}_2}$ : relative intensity of the third harmonic signal.

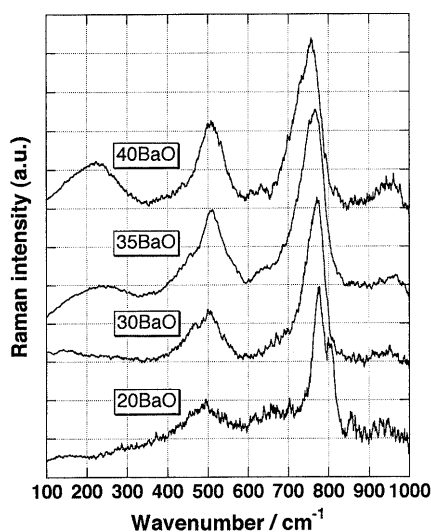


Fig. 1. Raman spectra of  $x\text{BaO} \cdot (100-x)\text{B}_2\text{O}_3$  binary glasses ( $x=20, 30, 35$  and  $40$ ).

a distinct peak is observed at  $800 \text{ cm}^{-1}$ . For  $40\text{BaO} \cdot 60\text{B}_2\text{O}_3$  glass, a broad peak is observed at ca.  $230 \text{ cm}^{-1}$ . For  $40\text{BaO} \cdot 60\text{B}_2\text{O}_3$  glass, weak bands appear at  $950$  and  $630 \text{ cm}^{-1}$ . With increasing BaO content, the intensity of the peaks at  $500$  and  $230 \text{ cm}^{-1}$  gradually increases and the peak at  $750\text{--}770 \text{ cm}^{-1}$  becomes sharper.

We next show the Raman spectra of  $\text{BaO-TiO}_2\text{-B}_2\text{O}_3$  ternary glasses in Fig. 2. The spectral profiles of these glasses are basically similar to each other and all the glasses show strong and broad peaks at  $830\text{--}850$  and  $330\text{--}350 \text{ cm}^{-1}$ . A peak is observed at  $700\text{--}720 \text{ cm}^{-1}$ . A weak peak at  $650 \text{ cm}^{-1}$  becomes evident with increasing  $\text{TiO}_2$  content. We also notice that with increasing  $\text{TiO}_2$  content, a peak at

Table 2. The Band Assignment of Raman Spectra for  $\text{BaO-TiO}_2\text{-B}_2\text{O}_3$  Glasses. Data Concerning Borate Groups are Cited from Ref. 18

Wavenumber / $\text{cm}^{-1}$	Activity	Assignments
940	Weak	Orthoborate group
850	Strong	$\text{TiO}_4$ unit
800	Strong	Boroxol ring
770	Strong	Tetraborate group
750	Medium	Diborate group
720-730	Weak	$\text{TiO}_5$ unit
650	Medium	$\text{TiO}_6$ unit
630	Weak	Metaborate groups
500	Weak	Isolated diborate group
320-350	Medium	$\text{TiO}_4$ and $\text{TiO}_6$ units
~230	Weak	Ba-O unit

$830\text{--}850 \text{ cm}^{-1}$  gradually become broader, and a peak at  $720\text{--}730 \text{ cm}^{-1}$  increases up to  $40 \text{ mol}\%$   $\text{TiO}_2$  and then decreases. The band assignment of  $\text{BaO-TiO}_2\text{-B}_2\text{O}_3$  ternary glasses is also listed in Table 2.

### 3.2 $^{11}\text{B}$ MAS NMR spectra

The  $^{11}\text{B}$  MAS NMR spectra taken at  $128 \text{ MHz}$  were used to determine the fraction of  $\text{BO}_4$  groups. Figure 3 shows the  $^{11}\text{B}$  MAS NMR spectra of  $\text{BaO-TiO}_2\text{-B}_2\text{O}_3$  glasses. A gaussian peak at  $0 \text{ ppm}$  is due to  $\text{BO}_4$  unit, and the fraction of the  $\text{BO}_4$  groups ( $N_4$ ) in the glasses can be estimated by integrating the peak areas after deconvolution. The  $N_4$  obtained as a function of BaO ( $x$ ) and  $\text{TiO}_2$  ( $y$ ) content is shown in Fig. 4. For  $\text{BaO-B}_2\text{O}_3$  binary glasses, the  $N_4$  increases from  $18.0\%$  ( $x=20$ ) to  $32.4\%$  ( $x=40$ ) with increasing BaO content. For  $35\text{BaO} \cdot y\text{TiO}_2 \cdot (65-y)\text{B}_2\text{O}_3$  ternary glasses, the  $N_4$  decreases from  $27.0\%$  ( $y=10$ ) to  $3.74\%$  ( $y=50$ ), and then becomes zero at  $55 \text{ mol}\%$   $\text{TiO}_2$ .

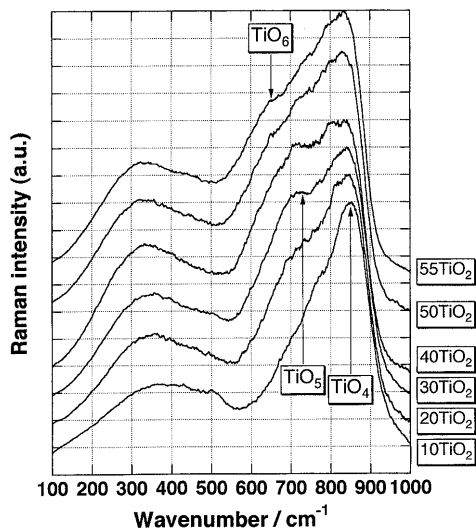


Fig. 2. Raman spectra of 35BaO·*x*TiO<sub>2</sub>·(65-*x*)B<sub>2</sub>O<sub>3</sub> ternary glasses (*x*=10, 20, 30, 40, 50 and 55). All the spectra are conventionally normalized to TiO<sub>4</sub> band.

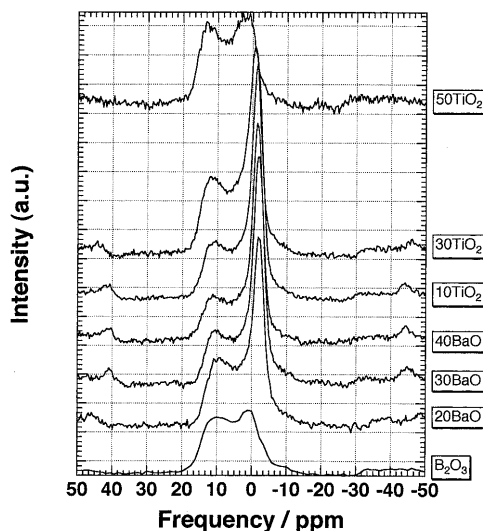


Fig. 3. <sup>11</sup>B MAS NMR spectra of *x*BaO·(100-*x*)B<sub>2</sub>O<sub>3</sub> binary (*x*=20, 30 and 40) and 35BaO·*y*TiO<sub>2</sub>·(65-*y*)B<sub>2</sub>O<sub>3</sub> ternary glasses (*y*=10, 30 and 50).

### 3.3 Linear and nonlinear optical properties

Transmittance (*T*), refractive index (*n*) and the optical band gap (*E<sub>g</sub>*) are listed in Table 1. The subscripts  $\omega$  and  $3\omega$  correspond to the wavelengths of 1.9  $\mu$ m and 633 nm, respectively. The refractive index at 1.9  $\mu$ m (*n<sub>ω</sub>*) was obtained from the extrapolation of  $1/(n^2-1)$  vs.  $E^2$  plots ( $E$ : photon energy) in accordance with Wemple's model.<sup>14)</sup>

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

where  $E_d$  is the dispersion energy and  $E_0$  is the oscillator energy. The values of  $E_d$  and  $E_0$  are listed in Table 1. In this table, the optical band gap ( $E_g$ ) of these glasses is also given. The optical band gap was estimated from the extrapolation of  $(AE)^2$  vs.  $E$  linear plot to the  $E$ -axis as seen in Fig. 5, where  $A$  is the absorption coefficient and  $E$  is the photon energy ( $h\nu$ ). The relationship between the optical band gap and the glass composition for BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses is plotted together with the refractive index-composition relationship in Fig. 6. For binary BaO-B<sub>2</sub>O<sub>3</sub> system,

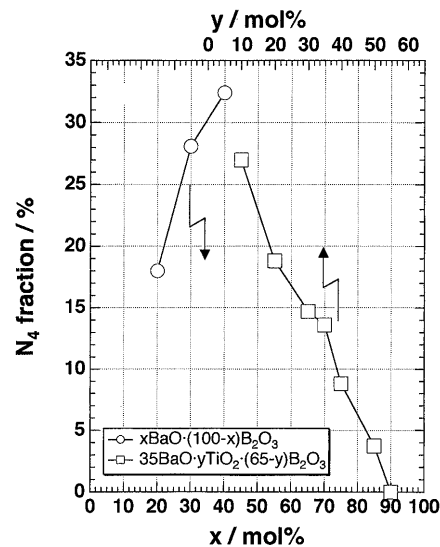


Fig. 4. N<sub>4</sub> fraction (%) of *x*BaO·(100-*x*)B<sub>2</sub>O<sub>3</sub> binary (*x*=20, 30 and 40) glasses (circle) and 35BaO·*y*TiO<sub>2</sub>·(65-*y*)B<sub>2</sub>O<sub>3</sub> ternary (*y*=10, 20, 30, 40, 50 and 55) glasses (square).

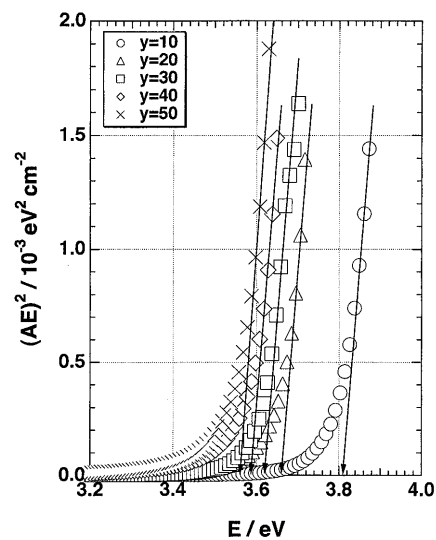


Fig. 5. Variation of  $(AE)^2$  with  $E$  in 35BaO·*y*TiO<sub>2</sub>·(65-*y*)B<sub>2</sub>O<sub>3</sub> ternary (*y*=10, 20, 30, 40 and 50) glasses. The optical band gap was estimated from the extrapolation of  $(AE)^2$  vs.  $E$  linear plot to the  $E$ -axis.

the optical band gap decreases from 7.2 eV for B<sub>2</sub>O<sub>3</sub> glass to 6.40 eV for 20 mol% BaO and then decreases to 6.01 eV for 40 mol% BaO with increasing BaO content. By substitution of 10 mol% TiO<sub>2</sub> for B<sub>2</sub>O<sub>3</sub>, the optical band gap decreases abruptly and remains almost unchanged with an increase of TiO<sub>2</sub> content. On the other hand, the refractive index increases more rapidly with increasing TiO<sub>2</sub> content compared with BaO-B<sub>2</sub>O<sub>3</sub> binary glasses.

The intensities of the third harmonic light in the BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses were measured. Figure 7 shows the third harmonic signal as a function of the incident angle for 35BaO·10TiO<sub>2</sub>·55B<sub>2</sub>O<sub>3</sub> glass. The THG intensity pattern of SiO<sub>2</sub> glass is also shown in this figure as reference. The detailed description of the calculation of the  $\chi^{(3)}$  value is made elsewhere.<sup>6)-8)</sup> The  $\chi^{(3)}$  values obtained are listed in the last column of Table 1. The relationship between  $\chi^{(3)}$  and the glass composition for BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses is plotted in Fig. 8. Although  $\chi^{(3)}$  increases with increasing

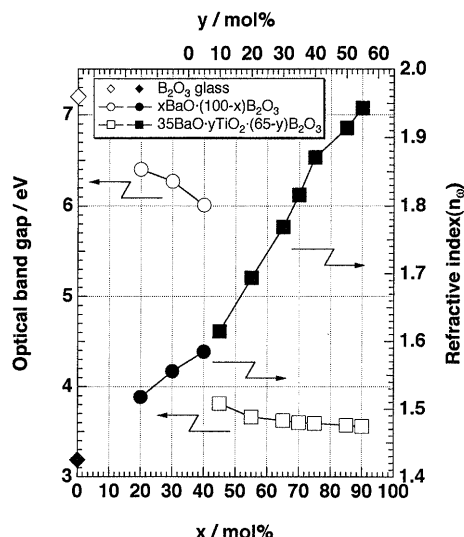


Fig. 6. The optical band gap (open marks) and the refractive index (full marks) as a function of the glass composition of BaO–B<sub>2</sub>O<sub>3</sub> binary (circle) and 35BaO·yTiO<sub>2</sub>·(65–y)B<sub>2</sub>O<sub>3</sub> ternary glasses (square).

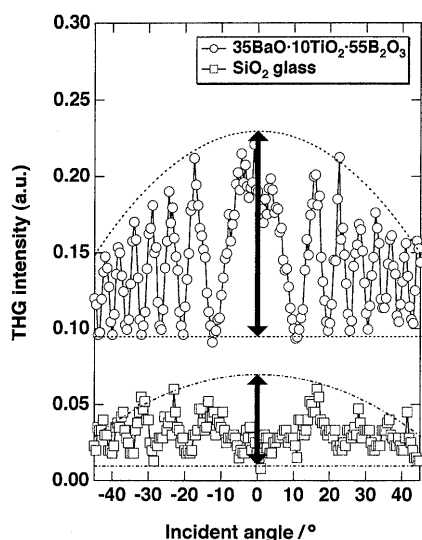


Fig. 7. The third harmonic intensity as a function of incident angle for 35BaO·10TiO<sub>2</sub>·55B<sub>2</sub>O<sub>3</sub> glass (circle) and the reference SiO<sub>2</sub> glass (square).

both BaO and TiO<sub>2</sub> content, the degree of enhancement of the  $\chi^{(3)}$  is much higher for TiO<sub>2</sub> than for BaO.

#### 4. Discussion

##### 4.1 Structure of BaO–B<sub>2</sub>O<sub>3</sub> binary and BaO–TiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> ternary glasses

There are several studies on the coordination states of Ti<sup>4+</sup> ions in alkali or alkaline earth titanate glasses. Sargeant and Roy,<sup>15)</sup> on the basis of IR spectra, considered that 4- and 6-coordinated Ti<sup>4+</sup> ions coexist in BaO–TiO<sub>2</sub> glasses which are made by the rapid quenching method. Miyaji et al.<sup>16,17)</sup> concluded that in the conventional and non-conventional glass matrices Ti<sup>4+</sup> ions exist as both 4- and 6-coordinated. Since the coordination state is closely related to the hyperpolarizability, it is of great importance to know the coordination state TiO<sub>n</sub> ( $n=4-6$ ) for a better understanding of the nonlinear optical properties. In this section, we first discuss the structure of BaO–B<sub>2</sub>O<sub>3</sub> binary and BaO–

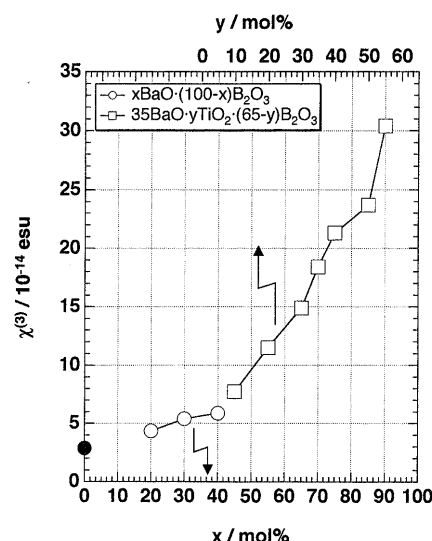


Fig. 8.  $\chi^{(3)}$  value as a function of glass composition of BaO–TiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> binary (circle) and 35BaO·yTiO<sub>2</sub>·(65–y)B<sub>2</sub>O<sub>3</sub> ternary glasses (square).

TiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> ternary glasses on the basis of the Raman and <sup>11</sup>B MAS NMR spectra.

According to the Raman spectra of  $x\text{BaO} \cdot (100-x)\text{B}_2\text{O}_3$  binary glasses ( $x=20, 30, 35$  and  $40$ ) in Fig. 1, 20BaO·80B<sub>2</sub>O<sub>3</sub> glass shows a prominent peak at 800 cm<sup>-1</sup> which is assigned to the boroxol-ring group. With increasing BaO content, this peak disappears and a band around 770 cm<sup>-1</sup> becomes broad with a shift to lower wavenumbers. The broadening of this band is attributed to the formation of tetra- and di-borate groups which contain one and two BO<sub>4</sub> tetrahedra, respectively, in the ring-type group.<sup>18,19)</sup> A broad band which appears at 500 cm<sup>-1</sup> is assigned to the isolated di-borate group.<sup>18)</sup> With increasing BaO content, this band sharpens and increases in intensity. The change in structural unit containing BO<sub>4</sub> tetrahedra is consistent with the change in  $N_4$  fraction as seen in Fig. 4. 40BaO·60B<sub>2</sub>O<sub>3</sub> glass shows a peak at 230 cm<sup>-1</sup> which is assigned to the stretching mode of Ba–O (displacement of oxygen). Note that such a oxygen means the non-bridging oxygen in BO<sub>3</sub><sup>-</sup> group formed by the addition of BaO.

As seen from the Raman spectra of 35BaO·yTiO<sub>2</sub>·(65–y)B<sub>2</sub>O<sub>3</sub> ternary glasses in Fig. 2, the bands due to the vibrations of the borate network units are obscure because of the high Raman scattering intensity of Ti–O vibrations. However, as seen from Fig. 4, it is obvious that the fraction of BO<sub>4</sub> decreases with increasing TiO<sub>2</sub> content. As shown in Fig. 2, a peak is seen in the high wavenumber region at 830–850 cm<sup>-1</sup>. Miyaji et al.,<sup>16,17)</sup> for several TiO<sub>2</sub>-containing glasses, assigned this band to the Ti–O symmetric stretching mode ( $\nu_1$ ) of TiO<sub>4</sub> tetrahedra. On the other hand, the peak at 650 cm<sup>-1</sup> which gradually increases with increasing TiO<sub>2</sub> content is assigned to the symmetric stretching mode of TiO<sub>6</sub> octahedra.<sup>17,20)</sup> It is, therefore, considered that TiO<sub>4</sub> and TiO<sub>6</sub> units coexist in the present Ti-containing glasses. It can be said that the fraction of TiO<sub>4</sub> tetrahedron is far larger than that of TiO<sub>6</sub> octahedron.

Yoshimaru et al.,<sup>21)</sup> on the basis of photoacoustic spectroscopies, reported that the fraction of 4-coordinated Ti<sup>4+</sup> ions increases with increasing basicity of glass. In the present system, in the low TiO<sub>2</sub> content region, the optical basicity is high and most of Ti<sup>4+</sup> ions exist as 4-coordinated. With increasing TiO<sub>2</sub> content, the TiO<sub>6</sub> fraction gradually increases.

In the low TiO<sub>2</sub> content region, the counter cation for the

non-bridging oxygen (NBO) of the borate network is Ba<sup>2+</sup> ion. With increasing TiO<sub>2</sub> content, the Ba<sup>2+</sup> ion which is in the vicinity of NBO is gradually replaced by Ti<sup>4+</sup> ion, then the NBO makes bond with Ti<sup>4+</sup> ion as Ti–O–B and the energy level of NBO gradually decreases. Since the basicity of the glass is principally dominated by the energy level of the NBO,<sup>22)</sup> the basicity decreases with increasing TiO<sub>2</sub> content.

One peak which is tricky is observed at 720–730 cm<sup>−1</sup>, which increases in intensity up to 40 mol% TiO<sub>2</sub> and then decreases. We assigned this peak to the Ti–O symmetric stretching mode of TiO<sub>5</sub> unit by the speculation from TiO<sub>4</sub> and TiO<sub>6</sub> modes.<sup>20)</sup> So far, several researchers indicated that the geometry of TiO<sub>5</sub> unit is considered to be a square pyramid as seen in crystals.<sup>23,24)</sup> For K<sub>2</sub>O·TiO<sub>2</sub>·2SiO<sub>2</sub> glasses, Yapker et al.<sup>25)</sup> concluded on the basis of the neutron diffraction and EXAFS analyses that 5-coordinated Ti<sup>4+</sup> ion takes a square pyramid geometry which has one titanyl-bond (Ti=O) at the apical site. Recently, Nasu et al. have indicated, on the basis of the second harmonic generation (SHG) of electrically-poled K<sub>2</sub>O–Cs<sub>2</sub>O–TiO<sub>2</sub>–SiO<sub>2</sub> glasses,<sup>26)</sup> that 5-coordinated Ti<sup>4+</sup> ion is in axial-symmetric geometry but not in a  $\sigma_h$  symmetry. It is, therefore, presumed that the geometry of TiO<sub>5</sub> unit in the glass is also a square pyramid. Since the optical properties of TiO<sub>5</sub> unit are expected to be rather similar to those of TiO<sub>6</sub> unit, we discuss the optical properties of the present glasses in terms of two criteria (TiO<sub>4</sub> and TiO<sub>6</sub> units) in the next section.

#### 4.2 Dependence of $\chi^{(3)}$ on the optical band gap

As previously reported by Hashimoto and Yoko,<sup>5)</sup> the  $\chi^{(3)}$  values of the TMOs with small optical band gap such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>, attained 10<sup>−12</sup>–10<sup>−11</sup> esu; these values are higher than that of SiO<sub>2</sub> by 2 or 3 orders of magnitude. This is mainly ascribed to the small optical band gap of TMOs because the band gap model<sup>5)</sup> predicts that a material with a small optical band gap has a high  $\chi^{(3)}$ . According to this model, it is hence expected that an enhancement of  $\chi^{(3)}$  occurs when a frequency of interacting light approaches either one-, two-, or three-photon resonance. The following equation has been obtained, assuming that the optical transition occurs between two levels and that the transition moment is constant.<sup>5,27)</sup>

$$\chi^{(3)} = \frac{\Phi}{(E_g - 3\omega) \cdot (E_g - 2\omega) \cdot (E_g - \omega)} \quad (2)$$

where  $\Phi$  is a phenomenological parameter. Figure 9 shows the relationship between  $\chi^{(3)}$  and the optical band gap for the present glass systems. In this figure, the  $\chi^{(3)}$  data of two TiO<sub>2</sub> polymorphs (i. e., rutile and anatase) which were investigated in the form of the sol-gel derived TiO<sub>2</sub> thin films, are also appended.<sup>10)</sup> A slightly higher  $\chi^{(3)}$  value of rutile compared with anatase is attributed to the higher refractive index and the narrower optical band gap of the former, which both arise from the broader Ti 3d conduction band as a result of the formation of the straight chains of TiO<sub>6</sub> octahedra in rutile, as distinct from the zigzag-chains of TiO<sub>6</sub> octahedra in anatase.<sup>10)</sup> It is clearly seen from Fig. 9 that  $\chi^{(3)}$  of BaO–TiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> glasses increases drastically at ca. 3.6 eV and deviates to a considerable extent from the values predicted by Eq. (2).

In the TiO<sub>n</sub> ( $n=4$ –6) units, the charge transfer preferably occurs for the unit with the smallest optical band gap. Since the LUMO level is primarily characterized by the Ti 3d anti-bonding orbital,<sup>28)</sup> it is considered that the TiO<sub>6</sub> unit with the longest Ti–O bond has the smallest optical band gap. In the low TiO<sub>2</sub> content glasses, the optical band gap decreases slightly by further addition of TiO<sub>2</sub> because most of the TiO<sub>n</sub> units are 4-coordinated. In the TiO<sub>2</sub> rich region,

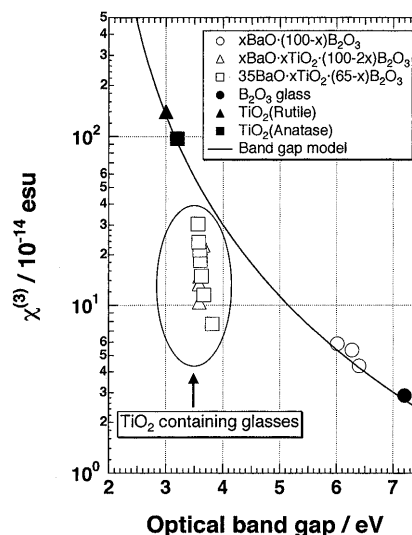


Fig. 9.  $\chi^{(3)}$  value as a function of the optical band gap ( $E_g$ ) for BaO–TiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> glasses. The solid line is the fitting curve based on Eq. (2).

however, the optical band gap would not be affected by further addition of TiO<sub>2</sub> because of the presence of some amount of TiO<sub>6</sub> units which determine the optical band gap. The optical band gap, therefore, remains almost unchanged. On the other hand, with increasing amount of Ti<sup>4+</sup> ions, the refractive index and the  $\chi^{(3)}$  increase because of the increase of the density of states (DOS) of acceptor levels which are determined by the amount of Ti<sup>4+</sup> ions.

For BaO–B<sub>2</sub>O<sub>3</sub> glasses, the optical basicity increases with increasing BaO content. The O 2p levels of NBOs increases with increasing optical basicity. Therefore, the  $\chi^{(3)}$  decreases with increasing the optical basicity. On the other hand, for BaO–TiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> glasses, the optical basicity decreases with increasing TiO<sub>2</sub> content, while the optical band gap slightly decreases. This result implies that the lowering of O 2p-orbitals of NBOs by the introduction of Ti<sup>4+</sup> is cancelled out by the lowering of acceptor levels consisting of Ti 3d anti-bonding orbitals.

The largest  $\chi^{(3)}$  obtained is  $3.0 \times 10^{-13}$  esu for 35BaO·55TiO<sub>2</sub>·10B<sub>2</sub>O<sub>3</sub> glass, which is, however, only 10 times larger than that for SiO<sub>2</sub> glass. Such small  $\chi^{(3)}$  values are attributed to the small fraction of the most polarizable TiO<sub>6</sub> unit. Since TiO<sub>4</sub> is the dominant unit even in high TiO<sub>2</sub>-containing glasses, the  $\chi^{(3)}$  is much smaller than those of TiO<sub>2</sub> polymorphs as seen in Fig. 9. It is, therefore, considered that TiO<sub>2</sub>-containing glasses will exhibit the higher  $\chi^{(3)}$  values when both lower optical basicity and large amount of Ti<sup>4+</sup> ion attained.

#### 4.3 $\chi^{(3)}$ on the basis of the modified Lines' bond orbital theory

In the previous section, we discussed the  $\chi^{(3)}$  dependence on the optical band gap. Such a band gap model did not hold well for the present glass systems. We tried to apply the semi-empirical Miller's rule, which is a well-known formula to discuss the relationship between the linear and nonlinear susceptibilities. This formula, however, also did fail to explain the results of the present glass system.

In order to investigate the relationship between  $\chi^{(3)}$  and the linear optical properties, here we introduce Lines' bond orbital theory.<sup>12,29)</sup> According to this theory, the  $\chi^{(3)}$  value is expressed by some measurable linear optical properties. This formula implies that  $\chi^{(3)}$  value is proportional to the term  $(n_\omega^2 + 2)^3 \cdot (n_\omega^2 - 1) \cdot d^2 / E_0^2$  at frequencies corresponding to  $(h\nu)^2 \ll E_g^2$ . It has been found that the  $\chi^{(3)}$  value esti-

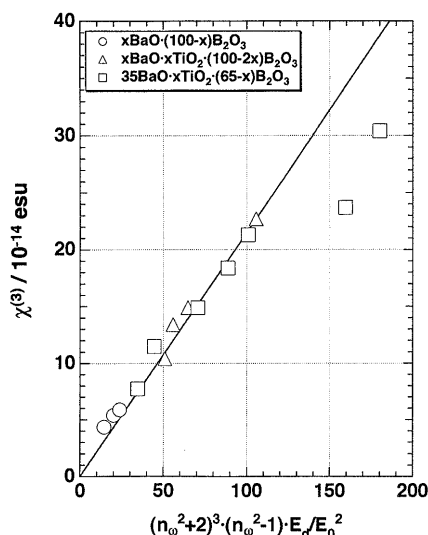


Fig. 10.  $\chi^{(3)}$  value as a function of the modified Lines' term  $(n_w^2 + 2)^3 \cdot (n_w^2 - 1) \cdot E_d / E_0^2$  for BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses.

mated from this term is in good agreement with the experimental one for TeO<sub>2</sub> glass.<sup>30</sup> However, this relation cannot be applied to the present binary glasses because it is difficult to evaluate experimentally the average Ti-O bond length ( $d$ ) for these glasses precisely. This problem may be solved by assuming that the dispersion energy ( $E_d$ ), which is derived by Wemple,<sup>14),31)</sup> is proportional to  $N_c \cdot d^2$ , where  $N_c$  is the coordination number around the metal cation. Assuming that  $N_c$  is constant,  $\chi^{(3)}$  can be expressed by Eq. (3).<sup>31)</sup> Hereafter, we call this relationship "modified Lines' equation."

$$\chi^{(3)} \propto (n_w^2 + 2)^3 \cdot (n_w^2 - 1) \cdot \frac{E_d}{E_0^2} \quad (3)$$

So far, this relationship has been found to be useful to calculate the theoretical  $\chi^{(3)}$  qualitatively and then to search the material with high  $\chi^{(3)}$ . Figure 10 shows the relationship between  $\chi^{(3)}$  and  $(n_w^2 + 2)^3 \cdot (n_w^2 - 1) \cdot E_d / E_0^2$  in BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses. It seems that this theory is in fairly good agreement with the observed points except for two high TiO<sub>2</sub>-containing glasses (i. e., 35BaO·50TiO<sub>2</sub>·15B<sub>2</sub>O<sub>3</sub> and 35BaO·55TiO<sub>2</sub>·10B<sub>2</sub>O<sub>3</sub>). Since this relationship is derived under the assumption that the  $N_c$  is constant,<sup>31)</sup> the deviation from the solid line may be attributed to the change in the coordination state around Ti<sup>4+</sup> ions from 4- to 6-coordinated as mentioned in Section 4.1.

### 5. Conclusion

The third order nonlinear optical susceptibilities  $\chi^{(3)}$  of BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses have been investigated by the third harmonic generation (THG) method. The structure of the present glasses has been discussed on the basis of Raman and <sup>11</sup>B MAS NMR spectra. The conclusions are as follows.

(1) The Raman spectroscopic study confirmed that Ti<sup>4+</sup> ions exist mainly as 4-coordinated and partly as 5- and 6-coordinated in the BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses.

(2) The largest  $\chi^{(3)}$  of this system is  $3.0 \times 10^{-13}$  esu for 35BaO·55TiO<sub>2</sub>·10B<sub>2</sub>O<sub>3</sub> glasses, which is only 10 times larger than SiO<sub>2</sub> glass. Such a small  $\chi^{(3)}$  is mainly ascribed to the dominant fraction of TiO<sub>4</sub> unit.

(3) It is considered that the optical band gap is determined by the formation of TiO<sub>6</sub> unit. On the other hand, the  $\chi^{(3)}$  is determined by the amount of net Ti<sup>4+</sup> ions.

(4) The  $\chi^{(3)}$  was found to change almost linearly with the modified Lines' term  $(n_w^2 + 2)^3 \cdot (n_w^2 - 1) \cdot E_d / E_0^2$  for

BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses when the term is relatively small.

(5) In the high TiO<sub>2</sub>-containing region, the observed points deviate from the modified Lines' linear relationship, which is attributed to the change in the coordination state around Ti<sup>4+</sup> ion from 4- to 6-coordinated.

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