Sol-Gel Preparation and Third-Order Optical Nonlinearity of Amorphous $\text{Bi}_2\text{O}_3\text{-TiO}_2$ and $\text{Nb}_2\text{O}_5\text{-TiO}_2$ Films

Hiroyuki NASU, Motohiko SATO, Jun MATSUOKA and Kanichi KAMIYA

Department of Chemistry for Materials, Faculty of Engineering, Mie University, 1515, Kamihama-cho, Tsu-shi 514

ゾル-ゲル法で得られた $\text{Bi}_2\text{O}_3\text{-TiO}_2$, $\text{Nb}_2\text{O}_5\text{-TiO}_2$ 非晶質膜の三次の非線形光学効果

那須弘行・佐藤元彦・松岡 純・神谷寛一

三重大学工学部分子素材工学科, 514 三重県津市上浜町 1515

Amorphous $\text{Bi}_2\text{O}_3\text{-TiO}_2$ and $\text{Nb}_2\text{O}_5\text{-TiO}_2$ transparent films were successfully prepared by dip coating method, using Bi-Ti complex alkoxide and corresponding metal alkoxide solutions, respectively. The films were amorphous up to 300 or 500°C and highly transparent from 500 to 2000 nm. The $\chi^{(3)}$ values obtained were mostly in the order of 10^{-12} esu although the films had high porosity, and the values of 10^{-11} esu were expected for fully dense amorphous films.

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1. Introduction

Generally, large third-order optical susceptibility ($\chi^{(3)}$) is observed in the materials with high refractive index. Thus, many efforts have been devoted to the preparation of the glasses with large refractive index.¹⁻³⁾ The largest $\chi^{(3)}$ for the bulk transparent glasses is in the order of 10^{-12} esu.¹⁾ Many of those glasses were prepared by traditional melting and quenching technique, and glass composition is limited by the several factors such as the stability and the viscosity of supercooled liquid and quenching rate. On the other hand, the sol-gel technique has been recently widely studied, in which amorphous and crystalline materials can be fabricated from solutions under ambient condition. The technique uses hydrolysis and polymerization of metal-organic compounds in solution at low temperatures, and thus high homogeneity and purity can be achieved. Further, the technique can extend glass forming region. Thus, the sol-gel technique can be considered to be useful to prepare and to tailor amorphous materials with high refractive index, which are difficult to obtain by the melting method. According to this concept, we previously reported the $\chi^{(3)}$ and the microstructure of the PbO-TiO_2 amorphous transparent monoliths derived by the sol-gel method,⁴⁾ and the $\chi^{(3)}$ values obtained were in the range of 5.7×10^{-13} to 1.4×10^{-12} esu. Hashimoto et al.⁵⁾ also used the sol-gel technique to prepare crystalline heavy metal oxides films and observed $\chi^{(3)}$ of 10^{-13} to 10^{-11} esu. These results show that the sol-gel technique is quite useful to obtain large $\chi^{(3)}$ materials. However, the influence of the addition of heavy metal oxides to amorphous films still remains not fully understood. Therefore, this paper reports the sol-gel preparation and third-order optical nonlinearity of the $\text{Bi}_2\text{O}_3\text{-TiO}_2$ and $\text{Nb}_2\text{O}_5\text{-TiO}_2$ amorphous films.

2. Experimental procedure

For $\text{Bi}_2\text{O}_3\text{-TiO}_2$ system, commercially available analytical grade $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Nacalai Tesque Inc.) and $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_4$ (Wako Pure Chemical Ind. Ltd.) were used as the starting materials. The flowchart for the preparation Bi-Ti complex alkoxide, which was a modification of the technique reported by Blum and Gurkovich,⁶⁾ is shown in Fig. 1. The starting compositions adopted were $10\text{Bi}_2\text{O}_3 \cdot 90\text{TiO}_2$, $20\text{Bi}_2\text{O}_3 \cdot 80\text{TiO}_2$, $30\text{Bi}_2\text{O}_3 \cdot 70\text{TiO}_2$ (mol%). Starting materials were weighed so that the total amount of complex was 0.1 mol. First, the dehydration of $\text{Bi}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was car-

ried out in a three-neck flask at 120°C under about 700 Pa for about 2h. Then, after exposed to ambient pressure, the $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_4$ was quite slowly put into the flask with 0.4 mol 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$). Subsequently, the solution was again heated to 120°C and refluxed for about 2h, and then the solution was cooled down to 50°C and distilled under 700 Pa to eliminate byproducts and unreacted 2-methoxyethanol. The Bi-Ti complex alkoxides of respective compositions were quite viscous and yellow transparent liquid. After cooled to room temperature, the liquid was diluted with 0.4 mol unhydrous ethanol and then acetic acid of 0.5 mol was slowly added. To the solution cooled in ice bath, the mixed solution of 0.2 mol distilled water and 0.4 mol ethanol was slowly added with stirring. The resultant solution was put into a polypropylene container as a coating solution.

For $\text{Nb}_2\text{O}_5\text{-TiO}_2$ system, commercially available analytical grade $\text{Nb}(\text{OC}_2\text{H}_5)_5$ and $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_4$ were used as starting materials. Prescribed amount of two alkoxides were mixed using unhydrous ethanol as a solvent. To the mixed alkoxide solution, $\text{H}_2\text{O-C}_2\text{H}_5\text{OH-HCl}$ solution was added for hydrolysis, according to the flowchart shown in Fig. 2. The molar ratio of the final solution for coating was alkoxides: $\text{C}_2\text{H}_5\text{OH} : \text{H}_2\text{O} : \text{HCl} = 1 : 20 : 2 : 0.05$. The $10\text{Nb}_2\text{O}_5 \cdot 90\text{TiO}_2$, $20\text{Nb}_2\text{O}_5 \cdot 80\text{TiO}_2$, $30\text{Nb}_2\text{O}_5 \cdot 70\text{TiO}_2$, $40\text{Nb}_2\text{O}_5 \cdot 60\text{TiO}_2$ and $50\text{Nb}_2\text{O}_5 \cdot 50\text{TiO}_2$ (mol%) compositions were selected.

For preparing coating films, SiO_2 glass substrates of 1 mm thick after cleaned well and carefully were dipped into the solution with a withdrawal speed of 0.15 mm/s. After dried for 10 min in the room temperature, the films were annealed at 300, 500 and 800°C for 10 min. This cycle was repeated for 10 times. At last, a SiO_2 film was coated to protect the films from the damage from high power laser and to avoid reflection at the surface during optical measurements. The SiO_2 film was dip-coated using the solution consisting of $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{C}_2\text{H}_5\text{OH}$ and H_2O in the molar ratio of 1: 5: 6 with the same withdrawal speed.

X-ray diffraction (XRD) patterns of the film specimens were recorded with Shimadzu XD-610 X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation as an X-ray source. Visible spectra were measured by Shimadzu UV-VIS-NIR spectrophotometer UV-3100. Refractive indices of the specimens were measured by ellipsometer (Mizoziri) DVA-36VW type in the wavelength range from 500 to

Fig. 1

Fig. 2

Fig. 3

Fig. 1. Flowchart for preparation of Bi_2O_3 - TiO_2 coating solution.Fig. 2. Flowchart for preparation of Nb_2O_5 - TiO_2 coating solution.Fig. 3. IR spectra of $20\text{Bi}_2\text{O}_3 \cdot 80\text{TiO}_2$ (mol%) gel and films heat-treated at indicated temperature.

1000 nm. The thickness of the coated films was measured from cross section of the films by scanning electron microscope (SEM) Hitachi S-2300. Infrared spectra (IR) were obtained by Nihon Bunko A-202 spectrometer to trace the residual organics from 400 to 4000 cm^{-1} in wavenumber, using the KBr pellet method.

Third-order optical nonlinearity was calculated from the intensity and coherent length of Maker fringe pattern of the third-harmonic generation (THG).⁷⁾ The THG values of the film specimens were measured using a pump wavelength of 1.9 μm generated from H_2 Raman shifter excited by a Q-switched Nd: YAG laser. The duration was 5.5 ns, the repetition rate was 10 Hz, and the peak power density was 200 MW/cm^2 . The detail of the measurement has been described elsewhere.⁸⁾

3. Results and discussion

3.1 Bi_2O_3 - TiO_2 films

Figure 3 shows the IR spectra of $20\text{Bi}_2\text{O}_3 \cdot 80\text{TiO}_2$ gel and the films heat-treated at 200, 300, 400, 500 and 600°C as a typical IR result. The absorption peaks in the range 1000–1600 cm^{-1} are assigned to unhydrolyzed acetate groups. The peaks disappear at 300°C. The water contamination (peaks at near 3500 and 1600 cm^{-1}) more or less is observed in all spectra because of using KBr pellets in the

measurement. The absorption peak over 400–800 cm^{-1} is assignable to Ti-O bonds. From these observations, one can say that residual organics are removed over 300°C.

XRD patterns of 10, 20, 30 mol% Bi_2O_3 -containing films annealed at 300 and 500°C are depicted in Figs. 4 (a) and (b), respectively. Although only broad patterns are seen in the Figs. 4(a) and (b). The crystalline species started to appear at 600°C, and the films heated from 300 to 500°C are considered to be amorphous oxides, with considering IR results.

From SEM analysis, the thickness of the film was 0.4 μm , and the surfaces were quite smooth for all specimens. No absorption and interference patterns were found over 500 to 2000 nm in visible and near IR spectra for the respective films.

Figure 5 shows a derived Maker fringe pattern for 300°C-treated amorphous $10\text{Bi}_2\text{O}_3 \cdot 90\text{TiO}_2$ film on a SiO_2 substrate, the output THG intensity observed is the mixed intensity of third harmonic generation from the films (I_{film}) and the substrate (I_{sub}) as follows;

$$I_{\text{film}} + I_{\text{sub}}/2 = (I_{\text{max}} + I_{\text{min}})/2 \quad (1)$$

where I_{max} and I_{min} are envelope maxima and minima of the oscillation, respectively, since I_{film} can not oscillate because of insufficient thickness to cause it. $\chi^{(3)}$ can be calculated from the following equation.

Fig. 4

Fig. 5

Fig. 4. XRD patterns of Bi_2O_3 - TiO_2 films heat-treated at 300°C (a) and 500°C (b).

Fig. 5. A typical Maker fringe pattern for the present films.

$$\chi^{(3)} = \frac{2}{\pi} \chi_s^{(3)} \frac{l_c}{l} \left(\frac{I_{3\omega}}{I_{3\omega,s}} \right)^{1/2} \left(\frac{n_{\omega}^3 n_{3\omega} T_{\omega,s}^3 T_{3\omega,s}}{n_{3\omega,s}^3 n_{\omega,s}^3 T_{\omega}^3 T_{3\omega}} \right)^{1/2} \quad (2)$$

where l , l_c , n , T , ω are the thickness, coherent length, refractive index, transmittance and frequency, respectively, and subscript s means the standard SiO_2 glass.^{9),10)}

Refractive index values at $1.9 \mu\text{m}$ (ω) and 633 nm (3ω), coherent length calculated from the frequency dependent refractive index, porosity, resultant $\chi^{(3)}$ values are tabulated in Table 1 for the films annealed at 300°C and in Table 2 for those annealed at 500°C . Porosity of the films were estimated on the basis of refractive index data using a following equation.¹¹⁾

$$P = 1 - \frac{n_1^2 - 1}{n_2^2 - 1} \quad (3)$$

where n_1 is the observed index and n_2 is calculated index for fully dense film using refractive indices of crystalline Bi_2O_3 and anatase. Although films contain still a large amount of pore, the derived $\chi^{(3)}$ values are close to 10^{-12} esu. As is seen, the annealing at 500°C densified the films and increased $\chi^{(3)}$. It is noteworthy that the $\chi^{(3)}$ of 2.5×10^{-12} esu for $30\text{Bi}_2\text{O}_3 \cdot 70\text{TiO}_2$ is comparable with those of fully dense anatase film (2.4×10^{-12} esu) and rutile (4.0×10^{-12} esu) film.⁵⁾ As well known, porosity reduces third-order non-linearity as well as refractive index.⁸⁾ Thus, it is interesting to calculate achievable $\chi^{(3)}$ for the fully dense films. As seen in Tables 1 and 2, the values are in the range of 10^{-11} esu, which is so far the largest $\chi^{(3)}$ among amorphous oxides, and basically increases as Bi_2O_3 content increases. However, $\chi^{(3)}$ values for the fully dense films may be overestimated because refractive indices of crystalline species are used to calculate the porosity. It implies that amorphous Bi_2O_3 - TiO_2 monoliths should have quite high potential to be very large $\chi^{(3)}$ materials.

3.2 Nb_2O_5 - TiO_2 films

XRD patterns of the films heat-treated at 300 and 500°C are shown in Figs. 6 (a) and (b), respectively. Only broad patterns are found in 300°C heated films. But for 500°C heated films, diffraction peaks assignable to TiO_2 (anatase) are noticed for the films containing TiO_2 over 70 mol%. However, the mean size of crystallite is calculated as 2–4 nm from the full width at the half maximum, and thus the

Fig. 6. XRD patterns of Nb_2O_5 - TiO_2 films heat-treated at 300°C (a) and 500°C (b).

Table 3. Refractive Index (n) at $1.9 \mu\text{m}$ (ω) and 633 nm (3ω), Coherent length (l_c), Porosity (P), Experimental $\chi^{(3)}$ (esu) and Estimated $\chi^{(3)}$ for Fully Dense Films Annealed at 300°C for Nb_2O_5 - TiO_2 Films

composition	$n_{3\omega}$	n_ω	$l_c(\mu\text{m})$	P(%)	$\chi^{(3)}(\text{esu})$	estimated $\chi^{(3)}$
$10\text{Nb}_2\text{O}_5 \cdot 90\text{TiO}_2$	2.24	2.13	2.9	32.7	9.9×10^{-13}	4.8×10^{-12}
$20\text{Nb}_2\text{O}_5 \cdot 80\text{TiO}_2$	2.26	2.15	2.9	28.7	1.0×10^{-12}	3.9×10^{-12}
$30\text{Nb}_2\text{O}_5 \cdot 70\text{TiO}_2$	2.30	2.19	3.0	23.5		
$40\text{Nb}_2\text{O}_5 \cdot 60\text{TiO}_2$	2.31	2.20	2.9	19.7	1.2×10^{-12}	2.9×10^{-12}
$50\text{Nb}_2\text{O}_5 \cdot 50\text{TiO}_2$	2.34	2.23	2.8	14.8	1.8×10^{-12}	3.4×10^{-12}

Table 4. Refractive Index (n) at $1.9 \mu\text{m}$ (ω) and 633 nm (3ω), Coherent Length (l_c), Porosity (P), Experimental $\chi^{(3)}$ (esu) and Estimated $\chi^{(3)}$ for Fully Dense Films Annealed at 500°C for Nb_2O_5 - TiO_2 Films

composition	$n_{3\omega}$	n_ω	$l_c(\mu\text{m})$	P(%)	$\chi^{(3)}(\text{esu})$	estimated $\chi^{(3)}$
$10\text{Nb}_2\text{O}_5 \cdot 90\text{TiO}_2$	2.26	2.15	2.9	31.2	1.2×10^{-12}	7.1×10^{-12}
$20\text{Nb}_2\text{O}_5 \cdot 80\text{TiO}_2$	2.35	2.22	2.4	28.7	1.2×10^{-12}	4.5×10^{-12}
$30\text{Nb}_2\text{O}_5 \cdot 70\text{TiO}_2$	2.41	2.29	2.4	14.2	1.3×10^{-12}	2.4×10^{-12}
$40\text{Nb}_2\text{O}_5 \cdot 60\text{TiO}_2$	2.41	2.30	2.9	11.0	2.0×10^{-12}	3.2×10^{-12}
$50\text{Nb}_2\text{O}_5 \cdot 50\text{TiO}_2$	2.43	2.31	2.8	6.57	1.9×10^{-12}	2.5×10^{-12}

Table 1. Refractive Index (n) at $1.9 \mu\text{m}$ (ω) and 633 nm (3ω), Coherent length (l_c), Porosity (P), Experimental $\chi^{(3)}$ (esu) and Estimated $\chi^{(3)}$ for Fully Dense Films Annealed at 300°C for Bi_2O_3 - TiO_2 Films

composition	$n_{3\omega}$	n_ω	$l_c(\mu\text{m})$	P(%)	$\chi^{(3)}(\text{esu})$	estimated $\chi^{(3)}$
$10\text{Bi}_2\text{O}_3 \cdot 90\text{TiO}_2$	2.06	1.92	2.3	46.1	1.0×10^{-12}	1.2×10^{-11}
$20\text{Bi}_2\text{O}_3 \cdot 80\text{TiO}_2$	2.01	1.87	2.3	48.6	1.0×10^{-12}	1.4×10^{-11}
$30\text{Bi}_2\text{O}_3 \cdot 70\text{TiO}_2$	1.95	1.83	2.6	51.3	9.7×10^{-13}	1.7×10^{-11}

Table 2. Refractive Index (n) at $1.9 \mu\text{m}$ (ω) and 633 nm (3ω), Coherent length (l_c), Porosity (P), Experimental $\chi^{(3)}$ (esu) and Estimated $\chi^{(3)}$ for Fully Dense Films Annealed at 500°C for Bi_2O_3 - TiO_2 Films

composition	$n_{3\omega}$	n_ω	$l_c(\mu\text{m})$	P(%)	$\chi^{(3)}(\text{esu})$	estimated $\chi^{(3)}$
$10\text{Bi}_2\text{O}_3 \cdot 90\text{TiO}_2$	2.20	2.04	2.0	36.2	1.7×10^{-12}	1.0×10^{-11}
$20\text{Bi}_2\text{O}_3 \cdot 80\text{TiO}_2$	2.12	1.98	2.3	40.9	1.8×10^{-12}	1.5×10^{-11}
$30\text{Bi}_2\text{O}_3 \cdot 70\text{TiO}_2$	2.07	1.95	2.6	43.0	2.5×10^{-12}	1.0×10^{-11}

films remain transparent. The thickness of the films was $0.3 \mu\text{m}$ from SEM observation.

Refractive index values at $1.9 \mu\text{m}$ (ω) and 633 nm (3ω), coherent length calculated from the frequency dependent refractive index, porosity, resultant $\chi^{(3)}$ values are tabulated in Table 3 for the films annealed at 300°C and in Table 4 for those annealed at 500°C . Just like the Bi_2O_3 - TiO_2 films, the heat treatment at higher temperature caused the densification of the films, resulting in higher $\chi^{(3)}$. The $\chi^{(3)}$ calculated for fully dense films is in the middle range of 10^{-12} esu, and the largest was 7.1×10^{-12} , which is comparable with that of As_2S_3 chalcogenide glass of large $\chi^{(3)}$. The increase of Nb_2O_5 content slightly lowers the calculated values.

4. Conclusion

Amorphous and transparent Bi_2O_3 - TiO_2 and Nb_2O_5 - TiO_2 films were successfully prepared by the sol-gel technique. For the Bi_2O_3 - TiO_2 system, after the heat treatment from 300 to 500°C , amorphous and residual organics-free oxide films were obtained. The $\chi^{(3)}$ ranges in the order of 10^{-12}

esu although the films have high porosity. It was expected that fully dense amorphous $\text{Bi}_2\text{O}_3\text{-TiO}_2$ compositions could have quite large $\chi^{(3)}$ in the range of 10^{-11} esu, which is the largest among amorphous oxides. For the $\text{Nb}_2\text{O}_5\text{-TiO}_2$ system, even the heat treatment at 500°C caused crystallization for some films with keeping transparency. $\chi^{(3)}$ of the films is in the range of 7.1×10^{-12} esu.

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