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Linear and nonlinear optical properties of single component Sb_2O_3 system

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단성분 Sb_2O_3유리의 선형 및 비선형 광학특성에 관한 연구

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Abstract A single component of Sb_2O_3 glass has been obtained by a rapid quenching method in vacuum. The linear refractive indices were measured as a function of wavelength from 500 nm to 1060 nm. The refractive index at $n_{3\omega}$(633 nm) was as high as 2.00. The optical band gap was estimated as 3.38 eV from the optical absorption spectrum. The third-order nonlinear optical intensity was determined by the third harmonic generation (THG) method. The $\chi^{(3)}$ value was as high as 5.68×10^{-13} esu, about 20 times larger than that of SiO_2 glass.

요 약 진공급냉법을 이용하여 단성분계 Sb_2O_3 유리를 제조하였다. 선형굴절율은 500-1000 nm 범위내에서 측정하였으며, 굴절율은 633 nm에서 2.0이었다. 에너지갭은 3.38 eV 이었으며, 3차 비선형 광학 감수율을 THG법을 이용하여 측정하였으며 단성분계 Silica 유리보다도 20배 큰 5.68×10^{-13} esu의 측정값을 얻었다.

1. Introduction

Conditional glass forming oxides such as PbO, Bi_2O_3 and Sb_2O_3 are of interest from the both structural and functional view points, especially in the field of optics. Since Kordes and Zachariasen's pioneering work [1,2] of Sb_2O_3 glass, some studies have been carried out on the structures [3-5] and physical properties of Sb_2O_3-containing binary glasses [6,7]. Very recently, structure of Sb_2O_3-B_2O_3 binary glasses has been reported

and their dielectric property was investigated by Gutenev et al. [8,9]. However, there are no systematic data of linear and nonlinear optical properties of single component Sb_2O_3, binary and ternary Sb_2O_3-based glasses, so far because Sb_2O_3 oxide form glass only under specific conditions. These facts stimulate us to prepare pure Sb_2O_3 glass and to investigate the fundamental optical properties, in order to establish a guide for Sb_2O_3-based glasses which may have a high 3rd-order nonlinear optical susceptibility, $\chi^{(3)}$

In the present work, we have tried to make pure Sb_2O_3 glass and measured various optical properties, such as refractive index and optical band gap, and the third-order nonlinear optical susceptibility $\chi^{(3)}$, of the glass. On the other hand, we discussed the relation between the covalency of Sb-O bond in the glass network and optical nonlinearity.

2. Experimental procedure

2.1. Preparation of glass

Sb_2O_3 of senarmontite as the starting material was melted in sealed, evacuated (8×10^{-5} torr.) silica ampoule with inner diameter 8 mm and wall thickness 1.2 mm at 750℃ for 20min. Sb_2O_3 glass was prepared by rapidly quenching the bottom of ampoule containing 3-5 g of glass melt using a freezing mixture consisting of ice, ethanol and NaCl kept at -11℃. The clear glass with a slightly yellowish color was obtained and annealed at 200℃ for 30min and then optically polished to eliminate a light scattering at the surface. The final thickness of Sb_2O_3 glass was 1.0 ± 0.05 mm.

2.2. Linear refractive index

The refractive indices were measured over a wide wavelength range from 500 to 1060 nm by an ellipsometer(Mizojiri Optical Works. model DVW-35VW). The refractive index at 1900 nm was estimated by extrapolating the linear plot of $1/(n^2-1)$vs.E^2(E= photon energy) as shown in previous report [10].

2.3. UV-Visible spectra

Spectra were measured in the wide wavelength region from 200 to 3000 nm by spectrophotometer (Hitachi model U-3500). The optical band gap E_g was estimated from the extrapolation of a linear portion of the $(\alpha h\nu)^2$ vs $h\nu$ plot to the $(h\nu)$ axis, where α is the absorption coefficient(cm^{-1}).

2.4. THG measurement

In order to obtain $\chi^{(3)}$ value, the 3rd harmonic generation intensity $I_{3\omega}$ was measured by THG method. The detailed procedures are shown in the previous work [11].

3. Results

Table 1

Linear and nonlinear optical properties of single component oxide glasses

Glass	$n_{3\omega}$	n_ω	d /Å	Abbe number	$T_{3\omega}$ /%	T_ω /%	E_0 /eV	E_d /eV	E_g /eV	$I_{3\omega}$ /a.u	l_c /μm	$\chi^{(3)}$ /10^{-13}esu
[a]Sb_2O_3	2.001	1.960	1.98	27.9	75.5	77.7	8.25	23.14	3.38	10.1	7.72	5.68
[b]TeO_2	2.184	2.121	2.01	28.5	62.8	67.5	6.85	23.70	3.37	13.2	5.03	14.10

a:Present work.

b:ref.11.

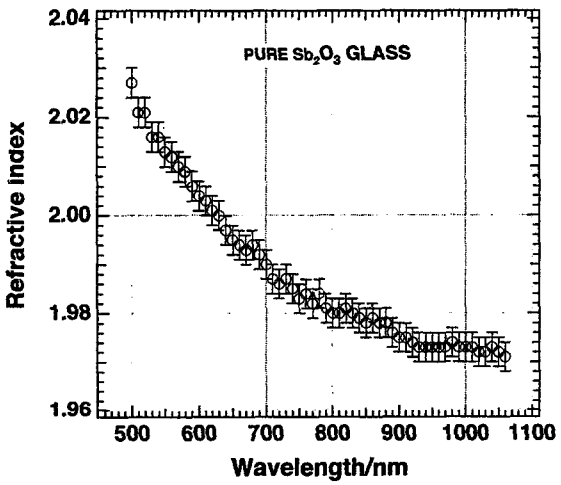

Fig. 1. Variation of refractive index with wavelength in Sb_2O_3 glass.

The wavelength dependence of the refractive index n of pure Sb_2O_3 glass is shown in Fig. 1. For comparison, the optical properties of pure TeO_2 glass [11] are also listed in Table 1. The refractive indicies decrease with increasing wavelength over a wavelength range from 500 to 1060 nm, showing the high value of about 2.0 at 633 nm as shown in Table 1. The refractive indices at 1.9 μm(n_ω) was extrapolated from the linear relationship between $1/(n^2-1)$ and E^2 [11]. From this result, in addition to the refractive indices at n_ω, the average excitation energy(E_0) and the electronic oscillator strength(E_d) [11], can be obtained. The values obtained for Sb_2O_3 glass are tabulated in Table 1.

Abbe number can also be calculated using the linear relationship between $1/(n^2-1)$ and E^2. The result is listed in Table 1.

The optical band gap (E_g) was estimated from the extrapolation of the a linear portion of the plot between$(\alpha h\nu)^2$ and$(h\nu)$, where α is the absorption coefficient(cm^{-1}) [11]. The values obtained are shown in Table 1.

The 3rd order nonlinear optical susceptibility $\chi^{(3)}$ was calculated from the 3rd harmonic generation intensity($I_{3\omega}$) using the following equation [11],

$$\chi^{(3)}_{sb_2o_3}=\chi^{(3)}_{sio_2}\times\frac{l_{c,\ sio_2}}{l_{c,\ sb_2o_3}}\sqrt{\frac{I_{3\omega,\ sb_2o_3}}{I_{3\omega,\ sio_2}}}\times f(n,T) \quad (1)$$

$$f(n,T)=\sqrt{\frac{T^3_{\omega,\ sio_2}\cdot T_{3\omega,\ sio_2}}{T^3_{\omega,\ sb_2o_3}\cdot T_{3\omega,\ sb_2o_3}}}\cdot\sqrt{\frac{n^3_{\omega,\ sb_2o_3}\cdot n_{3\omega,\ sb_2o_3}}{n^3_{\omega,\ sio_2}\cdot n_{3\omega,\ sio_2}}} \quad (2)$$

where the coherence length was calculated from the relation $l_c=\lambda_\omega l[6(n_{3\omega}-n_\omega)]$, where $n_{3\omega}$ and n_ω represent the refractive indices at 633 nm and 1.9 μm, respectively, and λ_ω is the wavelength of an incident beam. f(n, T) in eq. (2) is the correction factor. The relative intensity of the 3rd harmonic generation of silica glass used as a standard sample was estimated to be 1.0(a.u.) from the Maker fringe pattern. In the present study, the vallue of $\chi^{(3)}_{sio_2}=2.8\times10^{-14}$esu and the coherence length of 18.1 μm were adopted for SiO_2 glass used as the standard sample [12]. Figure 2 shows the relative intensity of the 3rd order harmonic generation of Sb_2O_3 glass as a function of incident beam angle from $-40°$ to $+40°$. The obtained values of n_ω, $n_{3\omega}$, $I_{3\omega}$ l_c, $_{sb_2o_3}$ and $\chi^{(3)}_{sb_2o_3}$ are summarized in Table 1. The obtained $\chi^{(3)}$ value of single component Sb_2O_3 glass is 5.68×10^{-13} esu.

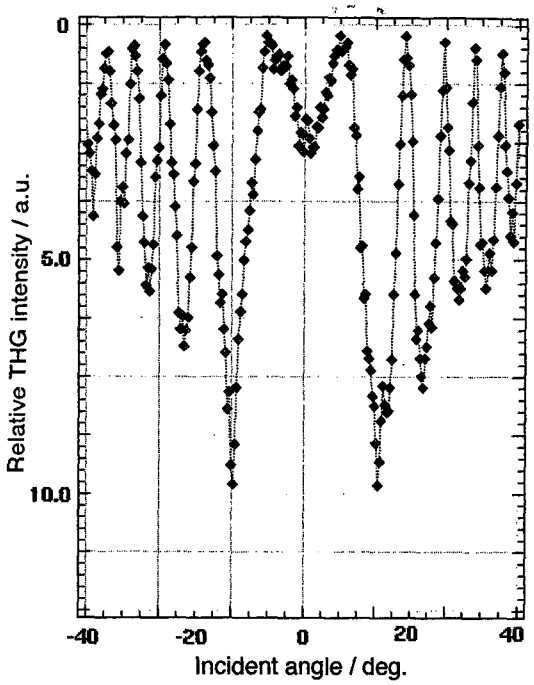

Fig. 2. Maker fringe pattern of Sb_2O_3 glass.

4. Discussion

The $\chi^{(3)}$ value of Sb_2O_3 glass is 5.74×10^{-13} esu which is smaller than that of 1.4×10^{-12} esu for pure TeO_2 glass [11]. Although Sb^{3+} and Te^{4+} have the same $d^{10}s^2$ configurations, both structure of the network of the TeO_2 and Sb_2O_3 glass are very different. The structure of pure Sb_2O_3 glass is a double chain consisting of four membered rings of SbO_3 pyramids similar to that of orthorhombic form valentinite, whereas TeO_2 glass consists of TeO_4 trigonal bipyramids, resembling that of tetragonal form paratellurite. On the basis of these facts, we made an attempt to discuss the difference between the $\chi^{(3)}$ value of Sb_2O_3 glass and that of TeO_2 glass.

In case of pure TeO_2 glass, the probable allowed optical transition in TeO_2 is the electron transfer from the non-bonding O $2p\pi$ orbitals to the empty non-bonding Te 5d orbitals by introducing the Lines'model based on the bond orbital theory [13,14]. In a similar manners the $\chi^{(3)}$ value of the pure Sb_2O_3 glass was calculated in order to investigate the influence of empty d- orbitals on the nonlinear optical response. The results are summarized in Table 2. This indicates that the contribution of empty 5d orbitals for Sb to the optical transition of Sb_2O_3 may not be significant because a reasonable agreement

Table 2

Comparison of the observed and calculated $\chi^{(3)}$ values for TeO_2 and Sb_2O_3 glasses at wavelength of 1.9 μm

Glass	f_L	f	E_S /eV	d /Å	$\chi^{(3)}/10^{-13}$ esu Cal.	Exp.
Sb_2O_3	1.947	1.71	8.25	1.98[b]	3.32	5.68
TeO_2	2.166	1.08	6.85	2.01[a]	11.20	14.10

a:ref.20.

b:ref.21.

Table 3

Individual bond strength-covalence parameters, bond-strength (S) and covalency(f_C) for Te, Sb-O bonds

Cation	S_0^a	R_0^b /Å	d(M-O) /Å	N^c	a^d	M^e	S cal.	f_C
Sb^{3+}	1.000	1.910	1.99	4.5	0.49	1.57	0.831	0.354
Te^{4+}	1.333	1.813	2.01	4.5	0.49	1.57	0.838	0.371

The data of a, b and c are cited from ref. 19.

The data of d and e are cited from ref.18.

is not obtained between the measured and calculated $\chi^{(3)}$ value for Sb_2O_3. In other words, the effects of degenerated 5d orbital for easy electron transfer may not be expected. The interaction of the filled Sb 5s and 5p atomic orbitals with the oxygen 2p orbitals forms molecular orbitals of σ-or π-bonds and this may lead to main optical transition because the energy level of oxygen 2p orbitals is in the vicinity of Sb 5s and 5p atomic orbitals [15]. However, it is very difficult and complicate to discuss the transition mechanism in detail because there is no data of MO theoretical calculation for these system.

On the other hand, here is to discuss the difference between Sb^{3+} and Te^{4+} in view of covalent character. The covalency is very closely related to the apparent optical band gap [16] on the basis of the highly covalent material having small optical band gap. Generally, the parameter as a covalent character is represented by R_m/V_m or metallicity [17], bond strength and covalency [18,19]. The empirical relationship between bond strength(S) and covalency(f_C) for bonds between oxygen and cations have been derived using a bond lengths and founded the linear relationships by Brown and Shannon [18]. The bond strength for M-O bonds can be described by

$$S=S_0\left(\frac{d}{R_0}\right)^{-N} \quad (3)$$

$$f_C = aS^M \quad (4)$$

where S and d are bond strength and mean bond length(M-O), respectively and S_0, R_0 and N are parameters for a given pair of ions, and a(=0.49) and M(=1.57) is determined by fitting curves of isoelectronic series. The calculated covalency values for Te^{4+} and Sb^{3+} and parameters [17,18] are summarized in Table 3. As a result, the covalency value of Sb^{3+}(0.354)is smaller than that of Te^{4+}(0.371). Although this calculation is very theoretical approach, the results of covalency value of Te^{4+} and Sb^{3+} could be used to predict the quantitative covalent character in glass network. In other words, the covalent character of TeO_2 may be larger than that of Sb_2O_3. Furthermore, Anderson et al. reported the distances between the lone pair center and the cation center of Te^{4+} or Sb^{3+} in the various structures [20]. They have calculated to be 1.17Å for Sb^{3+} and 1.32Å in the oxides. This result indicate that the probability of highly polarizable Te^{4+} cation may be higher than that of Sb^{3+}. On the basis of these facts, it is expected that the $\chi^{(3)}$ value of pure TeO_2 glass is higher than that of Sb_2O_3 glass from the facts that the optical band gap and excitation energy of Sb_2O_3 are higher than those of TeO_2 glass.

5. Conclusions

A pure Sb_2O_3 glass has been successfully obtained transparent glass by rapid quenching method in vacuum and measured various optical properties. The third-order nonlinear optical susceptibility c(3) of pure Sb_2O_3 glass was determined by the third harmonic generation (THG) method. The results obtained are as follows.

(1) The linear refractive index at n3w (633 nm) was as high as 2.00. The optical band gap was estimated as 3.38 eV from the optical absorption spectrum.

(2) The c(3) value of pure Sb_2O_3 glass was as high as 5.68×10^{-12}esu, about 20 times larger than that of SiO_2 glass but one-third the c(3) of TeO_2 glass.

(3) The difference between c(3)TeO_2 and c(3)Sb_2O_3 was discussed from the covalent character, the distances between the lone pair center and the cation center, the optical band gap, the excitation energy and the refractive index of both glasses.

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