Femtosecond measurement of third-order optical nonlinearities in Bi_2O_3-B_2O_3-BaO glasses

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We present the measurement of the third-order nonlinearity of Bi_2O_3-B_2O_3-BaO glasses using the single Z-scan method with femtosecond laser pulses at 750 − 850 nm. Both third-order nonlinear refraction γ and two photon absorption coefficient β are investigated. The γ shows an increasing tendency with increasing BaO content, and the largest value is estimated to be 7.2×10^{-14} cm^2/W, which is as large as those of chalcogenide glasses. The dependence of β on the normalized photon energy is studied.

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In recent years, materials with large third-order nonlinearity have been investigated extensively for their ability to be utilized in ultrafast all-optical switching in optical communication network[1,2]. For practical applications, optical solids are required to present large nonlinearity, low optical loss, and fast response time. Organic polymers exhibit large nonlinearity at their resonant wavelengths; however, they suffer large optical absorption and slow response time[3]. More recently, materials doped with nano-particles have been developed for their high optical nonlinearities that originated from resonance effect[4], but the preparation process of these materials is too complicated for mass production. Among these nonlinear optical materials, oxide glasses containing heavy metal oxide, such as PbO or Bi_2O_3, seem to be preferable candidates for constructing these optical systems[5,6], due to their large third order nonlinearity, fast response time, simple fabrication process, and high damage threshold.

In this letter, the third-order nonlinearities of Bi_2O_3-B_2O_3-BaO homogeneous glasses are measured by using the single Z-scan method at 750 − 850 nm. Nonlinear refractive index γ and two photon absorption coefficient β are investigated.

Reagent grade chemicals of Bi_2O_3, H_3BO_3, and $BaCO_3$ were used as starting materials. They were weighed to the nominal composition of $60Bi_2O_3$-$(40-x)B_2O_3$-xBaO (in mol%), where $0 \le x \le 15$ 30-g batches of powers were mixed and melted in platinum crucible in a SiC furnace at 1200 °C for 0.5 h in air. The melt was poured onto a stainless steel plate and annealed with a cool-down rate of 10 °C/h. The sample plates labelled as BBBx (x = 0,1,2,3) were cut and optically polished to a thickness of 1.5 mm for further measurement.

Refractive indexes n_0 of the samples were measured at the wavelength of 632.8 nm by using a SAIRON SPA4000 prism-coupler. As shown in Table 1, n_0 increases approximately from 2.035 to 2.078 as the BaO content increases. Note that n_0 increases rapidly when Ba^{2+} ions is incorporated into Bi_2O_3-B_2O_3 glass. We consider that this rapid increasing tendency is certainly caused by the structural changes induced in the glass network by the modifier cations. On the other hand, the increase of n_0 can be attributed to large cation polarizability of BaO (1.595×10^3 nm^3) which is much higher than that of B_2O_3 (0.002×10^3 nm^3)[7]. According to the Miller rule[8], high nonlinearity is expected with high linear refractive index. Its availability is discussed in the following paragraphs.

Absorption spectrum measurements over the range of 400 − 900 nm were performed by using a Perkin-Elmer-Lambda 950UV/VIS/NIR spectrophotometer. As can be seen in Fig. 1, these glasses show almost no optical absorption at the wavelength from 750 to 850 nm. Furthermore, the fundamental absorption edge $\lambda_{\rm off}$ of these glasses which results from the excitation of electrons from the upper edge of the valence band into the lower edge of the conduction band shifts from the short to the long wavelength side as the BaO content increases. According to the Tauc law[9], the optical band gap $E_{\rm opg}$ can be calculated as

$$\alpha h\nu = B\left(h\nu - E_{\rm opg}\right)^m, \tag{1}$$

where $h\nu$ is the incident photon energy, B is a constant that depends on the electronic transition probability, and the exponent m is a parameter which depends on the type of electronic transition responsible for the absorption. By extrapolating the linear portion of the curves to zero absorption, the $E_{\rm opg}$ values are determined. As shown in Fig. 2, the optical band gap is estimated to be 2.272 − 2.169 eV, and the value slightly decreases with increasing BaO content. As we know, in the Bi_2O_3 based glass system, the fundamental absorption edge is related to the

Table 1. Experimental Results of Examined Glass Samples

Sample	n_0 at 632.8 nm	$\lambda_{\rm off}$ (nm)	$E_{\rm opg}$ (eV)
BBB0	2.035	490	2.272
BBB1	2.067	504	2.237
BBB2	2.074	510	2.202
BBB3	2.078	524	2.169

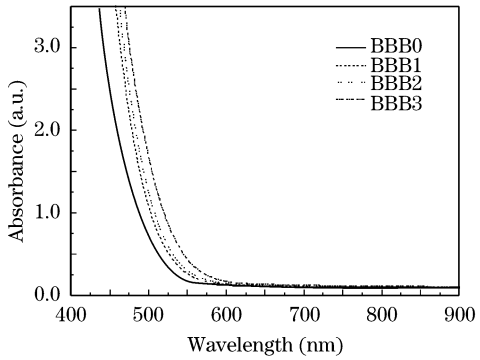

Fig. 1. Absorption spectra of BBBx (x = 0,1,2,3).

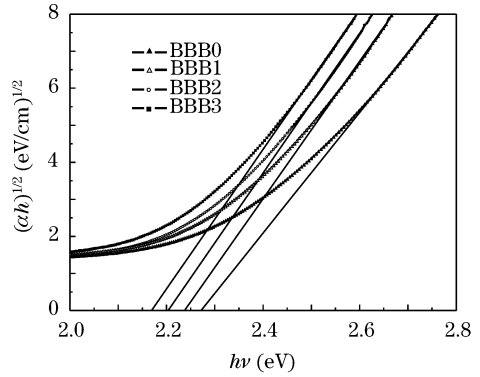

Fig. 2. Indirect allowed optical band gaps of BBBx (x = 0,1,2,3).

intra-atomic $6s \rightarrow 6p$ transition in Bi. However, transition from O $2p$ to Bi $6p$ with larger energy gap should also be considered[10]. In the present Bi_2O_3-B_2O_3-BaO system, when B_2O_3 is substituted by BaO mole by mole under constant Bi_2O_3 content, the oxygen molar volumes decrease, and a narrowing of optical band gap occurs consequently.

The nonlinear refraction γ and the nonlinear absorption coefficient β were measured by using femtosecond laser pulses generated form a Ti:sapphire laser (Coherent Mira 900-D) with the pulse duration of 200 fs. The laser pulses were operated at 76 MHz, and the wavelengths were ranged from 750 to 850 nm. The incident photon energy $h\nu$ was in the range of 1.48 − 1.67 eV, and the values of normalized photon energy at $0.5 < h\nu/E_{\rm opg} < 1$ were obtained, indicating that the nonlinear absorption mainly comes from two photon absorption. The closed aperture transmittance of a tightly focused Gaussian beam through a finite aperture S (linear transmission) in the far field was measured as a function of the sample position Z with respect to the focal plane. It should be pointed out that free carrier absorption and refraction are negligible when femtosecond pulses are used[11].

Figure 3 shows the typical result of Z-scan measurement for BBB3 at 800 nm. As can be seen in Fig. 3(a), the valley and peak of the experimental curve show asymmetric shapes. According to the method reported by Liu *et al.*[12], we easily separated nonlinear refraction and two photon absorption, and displayed them in Figs. 3(b) and (c), respectively. To estimate γ and β, the experimental data are fitted by

$$T(X) = 1 + \frac{4X}{(X^2+9)(X^2+1)}\Delta\Phi - \frac{2(X^2+3)}{(X^2+9)(X^2+1)}\Delta\psi, \quad (2)$$

$$X = \frac{Z}{Z_0} = \frac{2Z}{k\omega_0^2}, \quad (3)$$

where $\Delta\Phi = k\gamma I_0 L_{\rm eff}$, $\Delta\psi = \beta I_0 L_{\rm eff}/2$, $L_{\rm eff} = [1-\exp(-\alpha L)]/\alpha$, $k = 2\pi/\lambda$, L is the sample length, and α is the linear absorption coefficient. From theoretical fitting, the peak irradiance of the incident beams I_0 is 1.8 GW/cm^2, and the beam waist ω_0 is estimated to be 23 μm. In this case, γ and β of BBB3 at 800 nm are deduced to be 3.31×10^{-14} cm^2/W and 0.45 cm/GW, respectively. For the other glass samples measured at the wavelength range from 750 to 850 nm, the procedures are the same. The results are summarized in Table 2.

From the data of nonlinear refraction γ shown in Table 2, in the Bi_2O_3-B_2O_3-BaO glass system, there is an increase in γ with the addition of BaO. It should be noticed

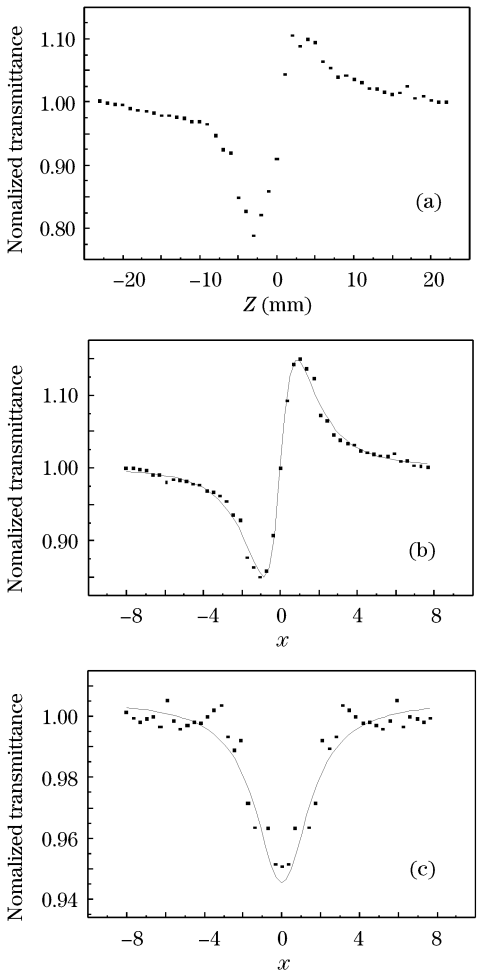

Fig. 3. (a) Closed-aperture Z-scan of BBB3 at 800 nm; (b), (c) separated transmittance curves due to nonlinear refraction and two photon absorption, respectively. The solid lines are theoretical fits.

Table 2. Nonlinear Parameters of Glass Samples in the Bi_2O_3-B_2O_3-BaO System

Sample (in mol%)	γ ($\times 10^{-14}$ cm^2/W)			β (cm/GW)		
	750 nm	800 nm	850 nm	750 nm	800 nm	850 nm
$60Bi_2O_3$-$35B_2O_3$-5BaO	0.974	0.826	0.709	0.530	0.306	1.963
$60Bi_2O_3$-$30B_2O_3$-10BaO	1.513	1.519	1.126	0.264	0.383	0.351
$60Bi_2O_3$-$25B_2O_3$-15BaO	7.200	3.313	1.783	0.170	0.448	0.657
$80GeS_2$-$10Ga_2S_3$ -$10CdI_2$[14]	–	0.75	–	–	–	–
90GeS-$5Ga_2S_3$-5CdS[15]	–	3.5	–	–	–	–

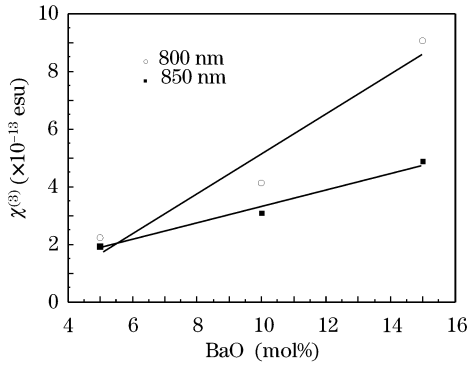

Fig. 4. $\chi^{(3)}$ as a function of BaO content at 800 and 850 nm. The solid lines are drawn as guides for the eye.

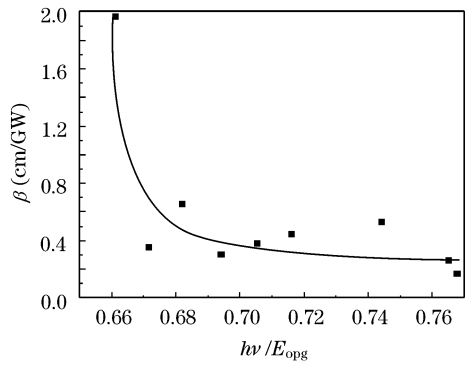

Fig. 5. Variation in the two photon absorption coefficient β with normalized photon energy $h\nu/E_{\rm opg}$. The solid line is theoretical fit.

that BaO incorporated into the glass Bi_2O_3-B_2O_3-BaO increases n_0 and decreases $E_{\rm opg}$, which is in good agreement with the previous works[13] that the third-order nonlinear refraction in glasses can be enhanced by maximizing linear refractive index n_0 and minimizing optical band gap $E_{\rm opg}$. Especially, $60Bi_2O_3$-$25B_2O_3$-15BaO has the largest value of γ at 750 nm, i.e., 7.2×10^{-14} cm^2/W. Then, its third-order optical nonlinear susceptibility $\chi^{(3)}$ is estimated to be 1.95×10^{-12} esu, which is as large as those of chalcogenide glasses[14,15].

It is known that the third-order nonlinear refraction in homogeneous glass is mainly due to electronic hyperpolarization, and the value of $\chi^{(3)}$ can be derived from the hyperpolarizabilities of glass constituents as[16]

$$\chi^{(3)}\left(-\omega;\omega_1,\omega_2,\omega_3\right)=\frac{L\left(\omega\right)L\left(\omega_1\right)L\left(\omega_2\right)L\left(\omega_3\right)}{24}\cdot\sum N_i\alpha_i^{(3)},\tag{4}$$

where $L(\omega)$ is the local field correction factor, N_i is the number density of the ith unit, α_i is the hyperpolarizability of the ith unit. In Z-scan measurement, Eq. (4) can be simplified as

$$\chi^{(3)}\left(-\omega;\omega,\omega,-\omega\right)=\frac{L\left(\omega\right)^4}{24}\sum N_i\alpha_i^{(3)}.\tag{5}$$

According to the previous report[17], Bi_2O_3 can be a network formed in B_2O_3 concentrated glass for the high polarizability of the Bi^{3+} cations. Nasu *et al.* have reported that the large $\chi^{(3)}$ found in Bi_2O_3 based glasses came from Bi-O-Bi bond and alkali ions[18]. In the present work, the increasing value of $\chi^{(3)}$ can be ascribed to the replacement of B_2O_3 with BaO. As mentioned above, the cation polarizability of BaO is 800 times higher than that of B_2O_3, Thus the influence of B_2O_3 reduction on $\chi^{(3)}$ can be negligible. Consequently, we anticipate that the increase of $\chi^{(3)}$ merely originates from the increasing number of Ba^{2+} ions in the present glass network, as shown in Fig. 4. Then, the average $\alpha^{(3)}$ of Ba^{2+} ions in the Bi_2O_3-B_2O_3-BaO glass system is estimated to be 8.9×10^{-36} esu cm^3/ion using Eq. (5). This value is smaller than those of K^+ and Rb^+, but larger than that of Na^+ in silicate glasses[16]. The large radius of Ba^{2+} ion is responsible for its large $\alpha^{(3)}$. Therefore, it is reasonable to enhance the $\chi^{(3)}$ of homogeneous glasses by addition of Ba^{2+} ions that possess strong hyperpolarizability.

From the two photon absorption coefficient β listed in Table 2, we note that β does not show obvious BaO content dependence, indicating the two photon absorption in Bi_2O_3-B_2O_3-BaO glass is governed by Bi, which is similar to the one photon transition in the fundamental absorption edge. Thus, we attempt to investigate the relationship between β and the normalized photon energy $h\nu/E_{\rm opg}$, since the two photon absorption in semiconductors is related to $h\nu/E_{\rm opg}$[19]. As shown in Fig. 5, it is of interest that β shows an increasing trend with the decreasing value of $h\nu/E_{\rm opg}$, and a steep edge around $h\nu/E_{\rm opg}\sim0.66$ is observed. The same phenomenon was also found in chalcogenide glass by Harbold *et al.*[20] Tanaka explained that the enhancement of two photon absorption processes could be attributed to the resonance effect from gap states[10], leading to our assumption that these resonant intermediate states were located at $h\nu/E_{\rm opg}\sim0.66$ in the present glass system. In other words, an enhancement of two photon absorption caused by the resonance effect will occur when the incident photon energy $h\nu$ approaches $0.66E_{opg}$ in the Bi_2O_3-B_2O_3-BaO glass system with a fixed Bi_2O_3 content.

In conclusion, large third order nonlinearities are found in Bi_2O_3-B_2O_3-BaO glasses using the Z-scan mehod with femtosecond laser pulses. The largest third order nonlinear susceptibility $\chi^{(3)} = 1.95\times10^{-12}$ esu in $60Bi_2O_3$-$25B_2O_3$-15BaO (in mol%) at 750 nm is obtained. The variation of β implies that the two photon absorption is determined largely by the resonance effect, and the resonance gap states appear at $0.66E_{\rm opg}$.

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