Femtosecond measurement of third-order optical nonlinearities in Bi$_2$O$_3$-B$_2$O$_3$-BaO glasses

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We present the measurement of the third-order nonlinearity of Bi$_2$O$_3$-B$_2$O$_3$-BaO glasses using the single Z-scan method with femtosecond laser pulses at 750 – 850 nm. Both third-order nonlinear refraction and two photon absorption coefficient are investigated. The γ shows an increasing tendency with increasing BaO content, and the largest value is estimated to be $7.2 \times 10^{-14}$ 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. 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. More recently, materials doped with nano-particles have been developed for their high optical nonlinearities that originated from resonance effect, 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$_2$O$_3$, seem to be preferable candidates for constructing these optical systems, 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$_2$O$_3$-B$_2$O$_3$-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$_2$O$_3$, H$_3$BO$_3$, and BaCO$_3$ were used as starting materials. They were weighed to the nominal composition of 60Bi$_2$O$_3$-(40-x)B$_2$O$_3$-xBaO (in mol%), where 0 $\leq$ x $\leq$ 15. 30-g batches of powders 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 BBB$x$ (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 are incorporated into Bi$_2$O$_3$-B$_2$O$_3$ 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 x 10$^{-21}$ cm$^3$) which is much higher than that of B$_2$O$_3$ (0.002 x 10$^{-21}$ cm$^3$). According to the Miller rule, 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 $\lambda_{off}$ 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, the optical band gap $E_{opg}$ can be calculated as

$$\alpha h\nu = B (h\nu - E_{opg})^m,$$

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 $E_{opg}$ 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$_2$O$_3$ based glass system, the fundamental absorption edge is related to the fundamental absorption edge $\lambda_{off}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n_0$ at 632.8 nm</th>
<th>$\lambda_{off}$ (nm)</th>
<th>$E_{opg}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBB0</td>
<td>2.035</td>
<td>490</td>
<td>2.272</td>
</tr>
<tr>
<td>BBB1</td>
<td>2.067</td>
<td>504</td>
<td>2.237</td>
</tr>
<tr>
<td>BBB2</td>
<td>2.074</td>
<td>510</td>
<td>2.202</td>
</tr>
<tr>
<td>BBB3</td>
<td>2.078</td>
<td>524</td>
<td>2.169</td>
</tr>
</tbody>
</table>

Table 1. Experimental Results of Examined Glass Samples
Fig. 1. Absorption spectra of BBB\(x\) \((x = 0, 1, 2, 3)\).

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

intra-atomic \(6s \rightarrow 6p\) transition in Bi. However, transition from O 2\(p\) to Bi 6\(p\) with larger energy gap should also be considered\[10\]. In the present Bi\(_2\)O\(_3\)-B\(_2\)O\(_3\)-BaO system, when B\(_2\)O\(_3\) is substituted by BaO mole by mole under constant Bi\(_2\)O\(_3\) content, the oxygen molar volumes decrease, and a narrowing of optical band gap occurs consequently.

The nonlinear refraction \(\gamma\) and the nonlinear absorption coefficient \(\beta\) 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 \(< h\nu/E_{opg} < 1\) 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 \(\gamma\) and \(\beta\), the experimental data are fitted by

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

where \(\Delta \Phi = k \gamma I_0 L_{\text{eff}}\), \(\Delta \psi = \beta I_0 L_{\text{eff}}/2\), \(L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha\), \(k = 2\pi/\lambda\), \(L\) is the sample length, and \(\alpha\) 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 \(\omega_0\) is estimated to be 23 \(\mu\)m. In this case, \(\gamma\) and \(\beta\) of BBB3 at 800 nm are deduced to be \(3.31 \times 10^{-14}\) 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 \(\gamma\) shown in Table 2, in the Bi\(_2\)O\(_3\)-B\(_2\)O\(_3\)-BaO glass system, there is an increase in \(\gamma\) with the addition of BaO. It should be noticed
that BaO incorporated into the glass Bi$_2$O$_3$-B$_2$O$_3$-BaO increases $n_0$ and decreases $E_{opg}$, which is in good agreement with the previous works\cite{11} that the third-order nonlinear refraction in glasses can be enhanced by maximizing linear refractive index $n_0$ and minimizing optical band gap $E_{opg}$. Especially, 60Bi$_2$O$_3$-25B$_2$O$_3$-15BaO has the largest value of $\gamma$ at 750 nm, i.e., $7.2 \times 10^{-14}$ cm$^2$/W. Then, its third-order optical nonlinear susceptibility $\chi^{(3)}$ is estimated to be $1.95 \times 10^{-12}$ esu, which is as large as those of chalcogenide glasses\cite{13,14}.

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\cite{15}

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

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

$$\chi^{(3)}(-\omega; \omega, \omega) = \frac{L(\omega)^4}{24} \sum N_i \alpha_i^{(3)}.$$  \hspace{1cm} (5)

According to the previous report\cite{17}, Bi$_2$O$_3$ can be a network formed in Bi$_2$O$_3$ concentrated glass for the high polariizability of the Bi$^{3+}$ cations. Nasu et al. have reported that the large $\chi^{(3)}$ found in Bi$_2$O$_3$ based glasses came from Bi-O-Bi bond and alkali ions\cite{18}. In the present work, the increasing value of $\chi^{(3)}$ can be ascribed to the replacement of B$_2$O$_3$ with BaO. As mentioned above, the cation polarizability of BaO is 800 times higher than that of B$_2$O$_3$. Thus the influence of B$_2$O$_3$ 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$_2$O$_3$-B$_2$O$_3$-BaO glass system is estimated to be $8.9 \times 10^{-36}$ 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\cite{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 $\beta$ listed in Table 2, we note that $\beta$ does not show obvious BaO content dependence, indicating the two photon absorption in Bi$_2$O$_3$-B$_2$O$_3$-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 $\beta$ and the normalized photon energy $hv/E_{opg}$ since the two photon absorption in semiconductors is related to $hv/E_{opg}$\cite{19}. As shown in Fig. 5, it is of interest that $\beta$ shows an increasing trend with the decreasing value of $hv/E_{opg}$, and a steep edge around $hv/E_{opg} \sim 0.66$ is observed. The same phenomenon was also found in chalcogenide glass by Harbold et al\cite{20}. Tanaka explained that the enhancement of two photon absorption processes could be attributed to the resonance effect from gap states\cite{20}, leading to our assumption that these resonant intermediate states were located at $hv/E_{opg} \sim 0.66$ 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 $hv$ approaches $0.66E_{opg}$ in the Bi$_2$O$_3$-B$_2$O$_3$-BaO glass system with a fixed Bi$_2$O$_3$ content.

\begin{table}[h]
\centering
\caption{Nonlinear Parameters of Glass Samples in the Bi$_2$O$_3$-B$_2$O$_3$-BaO System}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Sample (in mol%) & $\gamma$ ($\times 10^{-14}$ cm$^2$/W) & $\beta$ (cm/GW) \\ 
& 750 nm & 800 nm & 850 nm & 750 nm & 800 nm & 850 nm \\
\hline
60Bi$_2$O$_3$-35B$_2$O$_3$-5BaO & 0.974 & 0.826 & 0.709 & 0.530 & 0.306 & 1.963 \\
60Bi$_2$O$_3$-30B$_2$O$_3$-10BaO & 1.513 & 1.519 & 1.126 & 0.264 & 0.383 & 0.351 \\
60Bi$_2$O$_3$-25B$_2$O$_3$-15BaO & 7.200 & 3.313 & 1.783 & 0.170 & 0.448 & 0.657 \\
80GeS$_2$-10Ga$_2$S$_3$-10CdI$_2$ & -- & 0.75 & -- & -- & -- & -- \\
90GeS$_2$-5Ga$_2$S$_3$-5CdS & -- & 3.5 & -- & -- & -- & -- \\
\hline
\end{tabular}
\end{table}
In conclusion, large third order nonlinearities are found in Bi$_2$O$_3$-B$_2$O$_3$-BaO glasses using the Z-scan method with femtosecond laser pulses. The largest third order nonlinear susceptibility $\chi^{(3)} = 1.95 \times 10^{-12}$ esu in 60Bi$_2$O$_3$-25B$_2$O$_3$-15BaO (in mol%) at 750 nm is obtained. The variation of $\beta$ implies that the two photon absorption is determined largely by the resonance effect, and the resonance gap states appear at 0.66E$_{opg}$.

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