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Optical Properties of Bi_2O_3–TeO_2–B_2O_3 Glasses

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ABSTRACT

Glasses of the Bi_2O_3–TeO_2–B_2O_3 ternary system were developed and their linear and nonlinear optical properties were investigated. The absorption edges of these glasses were found to be 367–384 nm with a good transmittance in visible wavelength, although they exhibit the refractive indices as high as 1.98–2.12 at 633 nm. The absorption edges are quite steep and they are analyzed by the Urbach theory. The obtained Urbach energies of these glasses are 73–79 meV which are comparable to silica glasses. The high refractive index and its glass composition dependency are discussed according to the basics of the electronic polarizability and optical basicity. The high third order nonlinear susceptibility $\chi^{(3)} = 2.0 \times 10^{-12}$ esu at 800 nm was also obtained in the $36Bi_2O_3$–$18TeO_2$–$46B_2O_3$ glass.

1. Introduction

It is widely known that glasses containing heavy metal oxides show various attractive optical features, such as the high refractive index, high third-order optical nonlinearity and high transmittance in near-IR. Recently, multi-component oxide glasses containing, La_2O_3, Nb_2O_5, WO_3, PbO, TeO_2 and Bi_2O_3 have been commercially developed and manufactured to achieve the high refractive index. Generally, high refractive index glasses show coloring, if they have a refractive index as high as $n \sim 2$. This is mainly caused by the optical absorption edge which locates not in deep-UV but in near visible wavelength. Additionally, the transmittance spectrum of glasses is usually deteriorated around the absorption edge, therefore the high refractive index glasses show a yellowish or grayish coloring. It is commonly considered that this transmittance degradation near the absorption edge is induced by not only the impurity contamination [1], but also the structural glassy-disorder [2] or the valence change of the heavy metal cations [3,4]. Near the absorption edge, the refractive index and optical nonlinearity are significantly enhanced by the electronic resonance [5]. If the blue-shifted absorption edge ($\lambda < 400$ nm) and the high transmittance in visible wavelength are achieved simultaneously in high refractive index glasses, we can fully utilize the high refractive index and high optical nonlinearity even near the absorption edge.

The optical nonlinearity of high refractive index glasses have been studied in various types of glasses so far, such as Pb, Bi, Te containing oxide glasses and chalcogenide glasses[6–8]. Those glasses typically show the high refractive index ranging from 1.9 to 2.5 and excellently high third order nonlinear susceptibility up to $\chi^{(3)} \sim 10^{-11}$ esu. Since the optical nonlinearity of the glasses is also significantly influenced by the location of the absorption edge, the higher optical nonlinearity the glass shows, the deeper coloring it generally shows. Some of those glasses can be applied in the optical telecommunication wavelength as optical fibers, since they exhibit a good transmittance in near-infrared. On the other hand, the transmittance spectrum in near the absorption edge has hardly been studied ever especially in high refractive index glasses.

In the present study, we report the basic optical properties of the glasses of Bi_2O_3–TeO_2–B_2O_3 ternary system (BTB glass). We found that BTB glass has a quite steep absorption edge which is hardly seen in the conventional high refractive index glasses. The structure of the absorption spectra is analyzed according to the “Urbach rule.” Furthermore, as it can be easily expected from their high Bi_2O_3 and TeO_2 contents, the quite high refractive index and high optical nonlinearity are also confirmed. The refractive index and related optical properties are analyzed by the concept of the electronic polarizability and optical basicity.

2. Experimental setup

BTB glass samples studied in this work were prepared from the starting raw materials of Bi_2O_3, TeO_2 and H_3BO_3. In order to eliminate the impurity contamination, Bi_2O_3 and TeO_2 of 99.999% purity and optical grade HBO_3 were used. The raw materials were batched to yield 200 g of glasses and melted in a gold crucible for 1 h at 950 °C. The glass melt was stirred to be homogenized thoroughly. After the homogenization, the glass melt was poured onto a pre-heated carbon-mold and carefully annealed from 400 °C to room temperature at the cooling rate of −1 °C/min to remove the stress in the glass. The glass transition temperatures of BTB glasses are 380–430 °C from the DTA analysis with the experimental error of ±5 °C which mainly depends on the sample preparation for the DTA analysis. The typical dimension of the glass sample was about 50 mm × 50 mm × 10 mm. The glass plates of 1 mm and 2 mm thickness were cut and optically polished

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for the measurements. The transmittance spectra were measured by a PerkinElmer Lambda1500 spectrometer at room temperature. The refractive indices were measured by a prismcoupler (Metrikon 2100) at the wavelength 633, 1310 and 1550 nm. We measured the nonlinear susceptibility $\chi^{(3)}$ by the Z-scan method using Ti:Sapphire fs-laser pulses. The center wavelength, pulse duration and peak power of fs-laser were 800 nm, 100 fs and 2.2 GW/cm^2 respectively. The detailed experimental setup is described in our previous report [9].

3. Experimental results

3.1. Glass forming region

Fig. 1 shows the glass forming region of BTB glasses plotted in the scale of mol %. As a frontier work, Dimitoriev et al. has already reported the glass forming region of this ternary system [10]. Our result shows a good agreement with their report. The glass composition having Te>57 mol% was not investigated in this work, because many works had been already made in the high Te content glasses [11]. In the case of B_2O_3-rich composition, the glass could not be formed because of a phase separation. On the other hand, the devitrification was found by the crystallization of bismuth-borate in the Bi_2O_3-rich glass composition.

3.2. Transmittance spectra

Fig. 2a and b shows the typical transmittance spectra of BTB glasses prepared in this study. The sample thickness was 1 mm and the measurement was done at room temperature. The glass compositions are also indicated in the figure. The glasses containing Bi_2O_3 often show a reddish or yellowish coloring due to the Bi-reduction in the case of high temperature melting or corrosion of crucibles [1,3,4,12]. The suppression of coloring is achieved thanks to a low enough melting temperature and using a gold crucible. BI65.5 glass containing 65.5 mol% of Bi_2O_3 is also shown for the comparison [9]. BI65.5 was developed as a nonlinear optical glass used in optical telecommunication wavelength and no special care was taken for the visible transmittance. Compared to BI65.5, it can be seen that the transmittance spectra of BTB glass is dramatically improved. From the figure, it is indicated that high Bi_2O_3 content glasses show the red-shift of the optical absorption edge. In Fig. 3, the near-IR transmittance spectrum of $27Bi_2O_3$–$18TeO_2$–$55B_2O_3$ glass is shown. As seen in Figs. 2 and 3, BTB glass has a wide transmittance window 400<λ<2000 nm. Table 1 shows the list of the optical absorption edge of all the samples investigated in this work. Here, we represent the optical absorption edge as a 5% transmittance wavelength λ_5 in 1 mm sample thickness.

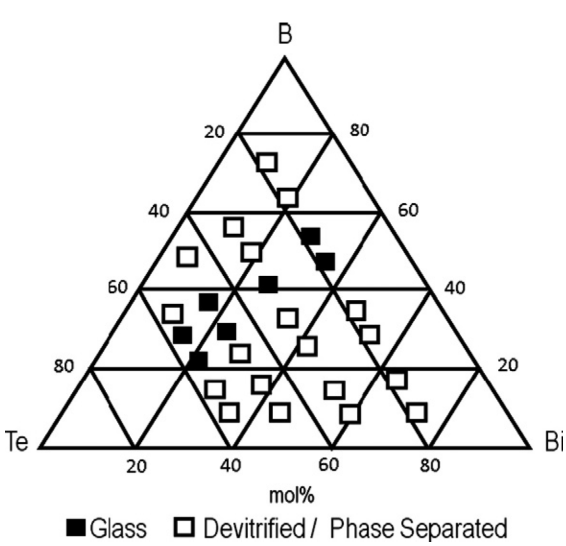

Fig. 1. Glass forming region of BTB glass in mol%. No investigation was done in Te>57 mol%.

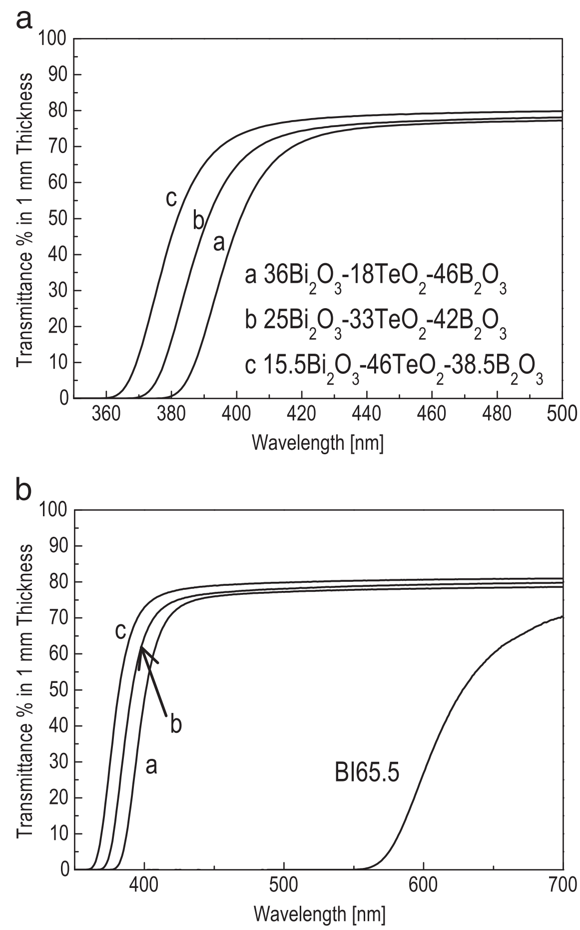

Fig. 2. Transmittance spectra of BTB glasses and BI65.5 [9]. a) Near the absorption edge, b) 350 nm–700 nm. The glass composition of BTB glasses is indicated in a).

3.3. Refractive index

Refractive indices of BTB glasses at 633, 1310 and 1550 nm are also listed in Table 1. The higher refractive index the glass has, the longer λ_5 it shows. This refractive index dependency on the absorption edge is found generally in the conventional optical glasses. It is noticeable

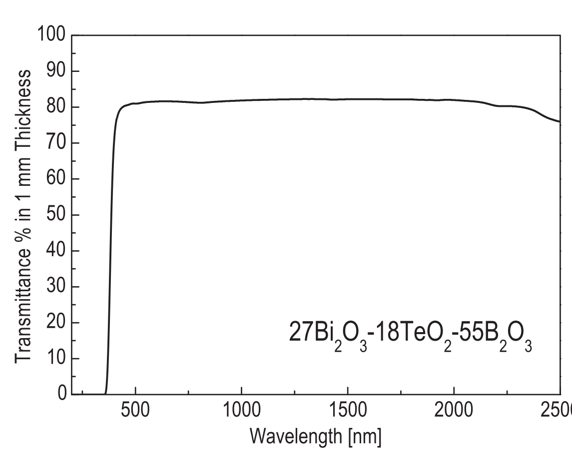

Fig. 3. Transmittance spectrum of $27Bi_2O_3$–$18TeO_2$–$55B_2O_3$ glass up to 2500 nm.