# High Refractive Index Bi<sub>2</sub>O<sub>3</sub>- B<sub>2</sub>O<sub>3</sub>-TeO<sub>2</sub> Glass with High Visible-NIR Transmittance

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**Abstract:** We have newly developed  $Bi_2O_3$ - $B_2O_3$ - $TeO_2$  glass system. This glass shows high transmittance in visible and near-IR wavelength, in spite of their high refractive index and optical nonlinearity.

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#### 1. Introduction

Generally, the third order optical nonlinearity of glasses strongly depends on their linear refractive index. It is well known that Ge-doping in silica glass enhances its refractive index, and Ge-doped silica fiber is used as a standard nonlinear medium in fiber optics. However, the refractive index of silica glass is intrinsically low, therefore non-silica glasses, e.g. chalcogenide, tellurite, and bismuth-based glasses, have been developed. This is because those glasses have significantly high refractive index  $n \sim 2$  in near-IR. In those glasses, chalcogenide glass and bismuth-based glass are developed with the expectation of applying in optical telecommunication. Consequently, those two glasses are deeply colored and they can not be used in visible wavelength. For example, bismuth-based glass developed for a high nonlinear optical fiber has absorption edge at  $\sim 600$  nm and the long absorption tail[1]. On the other hand, it is known that tellurite glass shows a relatively better transparency in visible wavelength in spite of its high refractive index[2]. It is also shown that tellurite glass photonic crystal fiber shows a relatively low  $\log \sim -1$  dB/m at 600 nm[3]. However, in those references, it is indicated that the absorption coefficient gradually increases toward the absorption edge near  $\sim 400$  nm. Since the optical resonance caused by electronic transition above the optical gap energy affects the refractive index in visible region, then, the refractive index is significantly enhanced near the absorption edge. Differently from crystals, glasses (except for high transparent silica) generally have long absorption tails induced by structural disorder, defects, impurities etc.. Therefore, in glasses, it is quite difficult to keep high transmittance at near absorption edge where we expect high refractive index. In this paper, we report on the linear and nonlinear optical properties of Bi<sub>2</sub>O<sub>3</sub> -B<sub>2</sub>O<sub>3</sub>-TeO<sub>2</sub> (BBT) glass containing Bi<sub>2</sub>O<sub>3</sub> and  $B_2O_3$  as main components and TeO<sub>2</sub> as an additional component. It is shown that BBT glass shows the high refractive index, high nonlinearity and excellent transmittance both in visible and near IR wavelength. The waveguide made of this glass is also shown.

## 2. Basic Properties

In Fig.1, the glass forming region of BBT glass is shown. The graph is plotted in cation %. We did not investigate the glass forming in TeO<sub>2</sub>>60 % region where the glass can be considered as tellurite glass. We obtained the glass blocks of which size were 80×40×15 mm after the careful annealing in the furnace (-60  $^{\circ}$  / hr). The glass forming region of our experiment is relatively narrower than that of reported by Dimitriev et al.[4]. This is probably due to the difference of the annealing condition. In this glass forming region, we found that BBT glass having  $30BiO_{1.5}$ - $60BO_{1.5}$ - $10TeO_2$  composition (BBT361) showed an excellent thermal stability, meaning that we can apply the redraw process on it to fabricate an optical fiber. Usually, in multi component glass systems, many additional elements are added into glass to maintain the



Fig. 1. Glass forming region (shaded area) of BTB glass system plotted in cation %, In TeO<sub>2</sub>>60%, no investigation was done in this work.



Fig. 2. Transmittance spectrum of BBT361. The sample thickness is 2 mm.

thermal and chemical stabilities. Then, it is interesting feature that BBT glasses are stable in spite of their simple glass composition. The transmittance spectrum of BBT361 (2 mm thickness) is shown in Fig. 2, indicating that this glass shows high transmittance from 400 nm to 2000 nm. The wavelength at the transmittance of 5% is 371 nm. It is important to point out that the high optical transmittance is maintained even near absorption edge (see the inset of Fig. 2). This means that the absorption tail is suppressed in the BBT glass, differently from other multi component glasses. Figure 3 represents the wavelength dependence of the linear refractive index of the BBT361. The refractive indices are 1.98 and 1.93 at 588 nm (d-line) and 1550 nm respectively. As mentioned above, glasses show poor transmittance in near the absorption edge where the refractive index rapidly enhanced. On the contrary, the BBT361 shows the enhancement of refractive index at near the absorption edge. The strong wavelength dependence of refractive index indicates that the chromatic dispersion is also significant. The material dispersion in visible wavelength is the order of -1000 ps/nm/km, which is extremely dispersive compared to other materials. The existence of chromatic dispersion is not favored in nonlinear optical applications because it disturbs the optical pulse propagation. However, this strong dispersion may be utilized as an optical delay or a pulse stretcher.

## 3. Optical Nonlinearity

The high refractive index glasses also show the high optical nonlinearity. We measured the nonlinear refractive



Fig. 3. Wavelength dependence of refractive index (solid line) and material dispersion (dashed line) of BBT361.

index (or nonlinear susceptibility  $\chi^{(3)}$ ) by Z-scan method using fs-laser pulses at 800 nm. The obtained nonlinear refractive index and nonlinear susceptibility at 800 nm were  $n_2=1.9\times10^{-18}$  m<sup>2</sup>/W and  $\chi^{(3)}=1.8\times10^{-12}$  esu. This nonlinear refractive index is about 60 times higher than that of silica, and comparable to the nonlinear refractive index of tellurite glasses reported so far.

## 4. Waveguide Fabrication

We fabricated waveguides made of BBT361 by the redraw process. The core-less waveguide was fabricated from the glass rod of BBT361. The diameters of fabricated waveguides were  $70 \sim 350 \ \mu\text{m}$ . The BBT glass has relatively low glass transition temperature ~400C°, indicating that it is easy to form the glass in fiber. In BBT361, the glass transition temperature is Tg=429 C°, and deformation point is At=460 C°. The redraw process was done slightly above At. Fig. 4 is the picture of the white-light generation (or super-continuum generation) observed in 350 µm diameter waveguide. The waveguide length was 20 mm. The seed pulse ( $\lambda$ =800 nm, 100 fs duration, 2 µJ/pulse) were induced into the waveguide via the objective lens. The input pulses were well attenuated to prevent the waveguide facet being damaged. The white-light scattered in the waveguide was observed. Unfortunately, the fabricated waveguide has many defects or cracks inside, the propagation loss is quite large. Therefore, the input pulses were attenuated significantly, and the white-light generation was observed only in the side of input. The improvement of fabrication process is necessary to observe more obvious nonlinear effects.

## 5. Conclusion

We have developed new glass system of which composition is  $Bi_2O_3$ - $B_2O_3$ - $TeO_2$ . This BBT glass shows high transmittance in wider wavelength region from 400 nm to 2000 nm. The refractive index of BBT361 is as high as 1.98 at 588 nm. It is a remarkable feature that this glass has sharp absorption edge without long absorption tail which is usually found in multi-component glasses. This high transmittance near the absorption edge leads the extraordinary large chromatic dispersion. The nonlinear refractive index at 800 nm was measured as  $1.9 \times 10^{-18}$  m<sup>2</sup>/W, indicating this glass has high nonlinearity, comparable to tellurite glasses reported so far.

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Fig. 4. White-light generation observed in BBT361 waveguide. The diameter of the waveguide is 350 µm.

#### 6. References

- T. Hasegawa, T. Nagashima and N. Sugimoto, "Z-Scan study of third-order nonlinearities in bismuth-based glasses," Opt. Comm., vol. 250, p.411, 2005
- [2] S-H Kim, T. Yoko and S. Sakka, "Linear and Nonlinear Optical Properties of TeO<sub>2</sub> Glass," J. Am. Ceram. Soc., vol 76, p.2486, 1993.
- [3] A. Mori K. Shikano, W. Enbutsu, K. Oikawa, K. Naganuma, M. Kato, and S. Aozasa, "1.5 □ m band zero-dispersion shifted tellurite photonic crystal fibre with a nonlinear coefficient □ of 675 W<sup>-1</sup> km<sup>-1</sup>", ECOC 2004, Stockholm, Sweden, Th3.3.6., 2004.
- [4] Handbook of Glass Data Part D, Elsevier, 1981