Fabrication of BaO–TiO2–GeO2–SiO2 based glass fiber

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The thermal properties of BaO–TiO2–GeO2–SiO2 based glasses have been investigated. The temperature differences, ΔT, between the crystallization onset temperature and glass transition temperature were over 95°C. The wide range of ΔT enables the fabrication of practical fibers with a core/clad structure including partial crystallization. The rod-in-tube method was used for fabricating fiber preform, and the fiber drawing was successfully achieved. The double clad fiber with the core diameter of 6.5 μm, the 1st clad diameter of 24.5 μm, and the 2nd clad diameter of 125 μm was obtained over 100 m in length. The propagation loss of the fiber was 1.8 dB/cm. The crystallization onset temperature of the 1st cladding is lower than other glass compositions, so that only the 1st cladding is selectively crystallized by post-heating for active devices. Furthermore, the 1st cladding contains CuO to assist heating by absorbing the energy of laser irradiation. Fusion splicing to the conventional silica fiber was also achieved, in spite of the different thermal properties of BTGS glass and silica glass, by precisely controlling the heating power and heating position of the fiber. The splicing loss with less than 1.5 dB per point was achieved.

Key-words : Optical fiber, Crystallization, Nonlinearity, BaO–TiO2–GeO2–SiO2

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1. Introduction

Much attention has been paid to nonlinear optical materials for the wavelength conversion, signal processing, switching, and so on. Although second-order nonlinear optical materials, LiNbO3 (LN), KTiOPO4, and β-BaB2O4 single crystals are well known, for the advanced fiber network systems, it is strongly desired to show the second-order nonlinearity in optical fibers for cost effectiveness and easy connection to the fiber systems. The conventional SiO2 based glass fiber does not show the second-order optical nonlinearity, because of the random structure of the glass with inversion symmetry. To induce the second-order optical nonlinearity in glass, poled silica fibers and waveguides have been demonstrated with the second-order optical nonlinearity.1)2) These results are based on a number of works with poled glasses, e.g., fused silica glass induced by electric-field poling process with elevated temperatures,3) and germanosilicate glass poled with ultraviolet irradiation,4) and so on. However, the second-order optical nonlinearity induced in poled glass is not enough for practical usage because of small amplitude and degradation of the nonlinearity. Prasad et al. studied glass fibers using nonlinear optical crystals with KTiOPO4 in tellurite based glass.5) However, the glass fiber with crystal was opaque.

Recently, transparent crystallized glasses with a large second-order optical nonlinearity have been developed in BaO–TiO2–SiO2 (BTS), and BaO–TiO2–GeO2 (BTG) based glasses.6)–10) Also, the transparent crystallized glass fiber with BTG crystals has been reported.11) The fiber was fabricated by pulling up the BTG glass from the melting glass. The transparent crystallized fiber was revolutionary, because the crystallized fiber has potential for both transmitting the optical waves in fiber and controlling the optical signals by second-order nonlinear effect. But the reported fiber was not designed for practical usage, because it was fabricated by pulling from the melting glass and lacked a core area. For practical usage to the network systems, it is required to propagate optical signals in core area of optical fibers. Also, the fusion-spooling is necessary for the reliability and easy introduction to the fiber systems. At present, these properties for the second-order nonlinear crystal fibers have not yet been achieved.

In this paper, we focus on fabrication of the practical fiber based on BaO–TiO2–GeO2–SiO2 (BTGS) glasses. The BTS and the BTG crystals are generated from BTS and BTG glasses, and they show the large second-order optical nonlinearity comparable to LN single crystal.12)–13) We have successfully fabricated a double clad fiber. The 1st cladding is designed for generating nonlinear crystals by a post-heating process. In addition, we show the fusion splicing ability in the case of the connection to the conventional silica fibers.

2. Experimental procedure

2.1 Fundamental properties of bulk glasses

Three types of BTGS based glasses were investigated with glass composition of 30BaO·15TiO2·30GeO2·25SiO2 (glass A), 30BaO·15TiO2·30GeO2·25SiO2·1CuO (glass B), and 30BaO·10TiO2·30GeO2·22SiO2·7X (glass C). Here, the X represents the sum of minor compositions. The BTGS based glasses were prepared by the conventional melting method. Batches were mixed and melted in a platinum crucible in the electric furnace at 1400°C. The liquid was then cast into the stainless mold. The obtained glass blocks were annealed at the temperature of glass transition (Tg) for 4 h, and cooled down to room temperature at the cooling rate of –1°C/min. The Tg and crystallization onset temperature (To) of the powdered glasses were measured by a differential thermal analysis (DTA) at the heating rate of 10 K/min using TG/DTA6300 (Seiko Instrument Inc.). Reflective indices of these glasses at 1550 nm were measured with a prism cou-
pler (Model 2010, Metricon Co.). Absorption spectra of these glasses with the thickness of 1.0 mm were measured using a UV–VIS–NIR recording spectrophotometer (U–3500, Hitachi, Ltd.). The viscosities were measured with a viscometer (WRVM–313, Opt Kigyo Co., Ltd.).

2.2 Fiber preparation and evaluation

The BTGS based glass fiber was fabricated as the process shown in Fig. 1. The rod-in-tube technique was utilized to prepare optical fiber preform. The rod for core glass was mechanically ground and polished from the glass block. The tubes for clad glass were drilled and polished on both the inside and outside of the surfaces. The glass C was used as the core glass. The core glass rod with a diameter of 15 mm was drawn to the diameter of 3.8 mm. The caning core rod was inserted into the jacket tube with outer diameter of 15 mm and inner diameter of 5.5 mm that forms the 1st cladding. The glass B was used as the 1st cladding. The core and 1st jacket tube were drawn with a heating temperature of 770°C to obtain the core-1st cladding rod. The rod was inserted into another jacket tube with an outer diameter of 15 mm and inner diameter of 4.5 mm that forms the 2nd cladding. The glass A was used as the 2nd cladding. The rod and 2nd jacket were drawn to the fiber preform. Finally, the fiber preform was drawn to the diameter of 125 μm with a heating temperature of 800°C. Over 100 m of BTGS glass fiber was obtained.

The BTGS based glass fiber was fusion spliced to a single mode silica fiber (980–HP, Nufern) with a conventional arc fusion splicer.

The cross-section of the fiber was measured by an optical microscope. The beam confinement in the core was confirmed by the near field pattern using a laser beam profiler (LEPAS–11, Hamamatsu Photonics K.K.). The propagation loss of fiber was measured by the cut-back method at 1550 nm.

3. Results

3.1 BaO–TiO2–GeO2–SiO2 (BTGS) based glasses

The DTA curves of three types of powdered glasses are shown in Fig. 2. The Tg and Tx of each glass were 707°C and 807°C for the glass A, 694°C and 789°C for the glass B, 706°C and 830°C for the glass C, respectively. The Tg of these glasses is almost the same. But the Tx of glass C is much higher than the other glasses, and that of the glass B is the lowest of these three glasses. The temperature difference between Tx and Tg of these glasses are over 95°C. The calorific values of glass B and glass C at the crystallization peak temperature were 1.8 times and 0.7 times larger compared to glass A. The refractive indices at 1550 nm of these glasses are 1.746 for glass A, 1.749 for glass B and 1.788 for glass C, respectively.

The absorption spectra of each glass are investigated. Figure 3 shows the absorption spectra. The glass A and glass B have no absorption band from 500 nm to 1550 nm. On the other hand, the glass B has a large absorption due to Cu ion at the peak wavelength around 790 nm. The peak absorption coefficient was 12.0
The absorption coefficient at the wavelength of 1060 nm and 1550 nm was 6.5 cm$^{-1}$ and 1.3 cm$^{-1}$, respectively. The effect of co-doping of CuO in glass B will be discussed in the next section.

The viscosity curves are shown in Fig. 4. At the processes of rod-in-tube and fiber drawing, the viscosity becomes important as the thermal property. The temperature of BTGS based glasses at the 10$^{15}$ dPa·s were 781°C (glass A), 790°C (glass B), and 767°C (glass C), respectively.

3.2 BTGS fiber

The cross-sectional image of the fiber is shown in Fig. 5. The diameters of core, 1st cladding and 2nd cladding were 6.5 μm, 24.5 μm and 125.0 μm, respectively.

We also investigated fusion splicing with BTGS fiber to silica fiber. The ends of the BTGS fiber and the silica fiber were heated by arc discharge using a conventional fusion splicer. However, the softening temperatures of the BTGS based glasses are less than 800°C, which is much lower than that of the silica glass over 1600°C. So we precisely controlled the arc discharge power and time. Also, the center position of a pair of electrodes was set to 350 μm offset from the end facet of silica fiber, not to heat BTGS fiber directly. Then the two fiber ends were pushed against each other. Figure 6 shows a picture of the splicing point. The process mentioned above was achieved by the successful fusion splicing of BTGS fiber to the silica fiber. The splicing points were reinforced with fiber protection sleeves (FPS01–400–12, Fujikura Ltd.).

Figure 7 shows the near field pattern from the facet of BTGS fiber. The light was inserted from the opposite end of the fiber. Fig. 7(a) shows the cross-sectional image of near field pattern. The dotted circle shows the outline of BTGS fiber. Fig. 7(b) shows the intensity profile at line A–B shown in Fig. 7(a). No clad mode was observed. It shows the light is propagating in the core area.

Figure 8 shows that the insertion loss of BTGS fiber fusion spliced to silica fiber. The loss at the wavelength of 1550 nm was plotted as a function of BTGS fiber lengths. The slope was –1.8 dB/cm, and the interception was –3.0 dB. So, the background loss of BTGS fiber was estimated to be 1.8 dB/cm, and the splicing loss was 1.5 dB per splicing point.

4. Discussion

4.1 BTGS based glass properties

The large nonlinearity of BTG crystals in transparent crystallized glass was reported.$^{6-8}$ The temperature difference ($\Delta T$) between $T_c$ and $T_g$ is small for the fiber fabrication.$^6$ The $T_c$ and $T_g$ were reported as 674°C and 721°C of 30BaO·15TiO$_2$·55GeO$_2$ glass. The small $\Delta T \sim 47$°C would be the reason for easy crystallization. But, as far as fiber fabrication, it brings the crucial issue of crystallization while drawing. The fiber with surface crystals would be fragile and difficult to treat. On the other hand, BTS glasses show a relatively large $\Delta T$.$^{10}$ The second-order nonlinearity, $d$ value, of BTS crystals has been reported to be 13 pm/V, that is a little bit smaller than that of BTG crystals with 22 pm/V, but it is still a large value.$^7$ The BTGS glass formation and single crystal was confirmed by Iijima et al.$^{12}$ To achieve both large nonlinearity and stable fabrication of the fiber, the BTGS glass systems are suitable. The $\Delta T$ of glass A, with the composition of 30BaO·15TiO$_2$·50GeO$_2$·5SiO$_2$, is 100°C. This larger $\Delta T$ allows the fabrication of practical optical glass fibers.

The glass B containing CuO shows the absorption by Cu ion.
It will assist crystallization of the glass with post-treatment of the fiber. The technique for laser induced writing of nonlinear optical single-crystal lines in rare earth doped and transition metal doped glasses has been developed by Honma et al.\textsuperscript{13,14} The rare earth or transition metal is heated by absorbing the laser energy and dissipated to the lattice with non-radiative relaxation. So a larger absorption coefficient at the wavelength of laser irradiation is required. Nowadays, the YAG laser or Yb-doped fiber laser is a concise procedure. The glass B with a large absorption of 6.4 cm\(^{-1}\) at 1060 nm would be preferred for the crystallization of the glass with laser irradiation.

4.2 Optical properties of BTGS based fiber

The connection of BTGS fiber to the conventional silica fiber was successfully fusion spliced with low loss. One of the origins of the splicing loss is the mismatch of the mode field diameter (MFD). The MFD of BTGS fiber is calculated to be 5.2 μm, and that of silica fiber used here was 6.8 μm. The loss of MFD mismatch is estimated to be 0.31 dB. The reflection loss is estimated to be 0.03 dB. The deformation of the fiber facets and misalignment are also supposed to affect the splicing loss.

The propagation loss of BTGS fiber is not enough small. The confinement factor of light in a core area was 0.95 assuming that the fundamental mode is the Gaussian profile, that means 5% of light is propagating at the 1st clad area. The absorption coefficient of glass B that is used at 1st cladding was 0.13 cm\(^{-1}\) (6.2 dB/cm) at 1.55 μm. From the confinement factor and absorption coefficient, propagation in the core is estimated to be 0.31 dB. The loss of bulk fiber of glass A is also investigated to check the glass loss, and the value was less than 0.1 dB/cm. The excess loss is supposed to be originated from surface defects, e.g., microcrystal, because the drawing temperature was higher than the T\(_{c}\) of glass B. To reduce the propagation loss, it will be required to improve the glass with a lower T\(_{c}\), adjusting the absorption material concentration (here CuO) or substitute other compositions, and fiber structure like a double core profile.

The propagation mode of the light in fiber is mainly determined by the index profile and core diameter. So conventional glass fiber is an optically “passive” material. If the optically nonlinear crystals are contained in the core or cladding, the fiber will be converted to an “active” component. The T\(_{c}\) of 1st clad glass of BTGS fiber is lower than that of core and 2nd clad glasses. The calorific value of the exothermic peak of 1st clad glass is the highest of other glasses. This shows that the 1st cladding can be selectively crystallized by heat treatment. Also, the absorption by Cu ion in the 1st clad glass will assist crystallization by laser irradiation. The crystallized glasses of BTG and BTS show a large second-order optical nonlinearity, thus the selectively crystallized BTGS fiber is expected to show large nonlinearity as well. Therefore BTGS fiber will be a candidate for active devices, and more studies would be reported following further research.

5. Conclusions

We have developed a double clad fiber using BaO–TiO\(_2\)–GeO\(_2\)–SiO\(_2\) based glasses for active devices. The thermal properties of three types of BTGS based glasses have been investigated. The T\(_{c}\) of the glass for the 1st cladding is the lowest than that of core and 2nd clad glasses. Also, the glass for the 1st cladding contains CuO to assist crystallization by absorbing the energy of the laser and heating the glass for selective crystallization. The preform with core/clad structure was fabricated employing the rod-in-tube method, and successfully drawn to fiber with 125 μm diameter. The fusion splicing BTGS based fiber to conventional silica fiber has been developed. The BTGS fiber, with an excellent ability of fusion splicing is a candidate for practical devices. The advanced research in relation with device characterization is in progress, and the results will be reported elsewhere.

References