Effect of Zn Addition on Non-Resonant Third-Order Optical Nonlinearity of the Cu-Doped Germano-Silicate Optical Glass Fiber

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Cu/Zn-codoped germano-silicate optical glass fiber was manufactured by using the modified chemical vapor deposition (MCVD) process and solution doping process. To investigate the reduction effect of Zn addition on Cu metal formation in the core of the Cu/Zn-codoped germano-silicate optical glass fiber, the optical absorption property and the non-resonant third-order optical nonlinearity were measured. Absorption peaks at 435 nm and 469 nm in the Cu/Zn-codoped germano-silicate optical glass fiber were attributed to Cu metal particles and ZnO semiconductor particles, respectively. The effective non-resonant optical nonlinearity, $\gamma$, of the Cu/Zn-codoped germano-silicate optical glass fiber was about four times larger than that of the reference germano-silicate optical glass fiber without any dopants. The increase of the effective non-resonant optical nonlinearity, $\gamma$, of the Cu/Zn-codoped germano-silicate optical glass fiber, can be attributed to the enhanced nonlinear polarization due to incorporated ZnO semiconductor particles and Cu metal ions in the glass network. The Cu/Zn-codoped germano-silicate optical glass fiber showed high nonlinearity and low transmission loss at the optical communication wavelength, which makes it suitable for high-speed-high-capacity optical communication systems.

Keywords: Germano-Silicate Optical Glass Fiber, Optical Absorption, Nonlinearity, Nonlinear Polarization, Metal Particles, Metal Ions, Semiconductor Particles, Optical Communication.

1. INTRODUCTION

The internet access networks for high-speed optical data transmission rate exceeding 100 Gbit/s require development of optical communication systems with high performance optical device technologies such as optical time division multiplexing (OTDM), wavelength division multiplexing (WDM), dense WDM (DWDM), and optical cross-connnect (OXC). Recently, highly non-resonant nonlinear optical fibers using intrinsic polarization or hyper-polarization properties have attracted much attention for ultra-fast all-optical communication devices applications such as all-optical switch, wavelength converter, ultra-short pulse generator, and optical parametric amplifier because of its fast response time and low absorption at the optical communication wavelength. Our group had earlier demonstrated highly non-resonant nonlinear optical fibers incorporated with Si nanocrystals, Cu ions, Pb ions, and Te ions due to their large inherent nonlinear polarizability. These fibers have also shown low splicing loss with commercial single mode fiber and low transmission loss at the optical communication wavelength, which makes it suitable for high-speed-high-capacity optical communication systems as compared with specially designed glass optical fibers such as small-core fiber and photonic crystal fiber.

In this paper, we report the fabrication of Cu-doped and Cu/Zn-codoped germano-silicate optical glass fibers by using the modified chemical vapor deposition (MCVD) process and the fiber drawing process. Especially, the effect of Zn codoping with Cu metal ions in the fiber
core on the formation of Cu metal particles and the subsequent change in non-resonant third-order optical nonlinearity, measured by using the continuous-wave self-phase modulation (SPM) method, was investigated.

2. EXPERIMENTAL DETAILS

2.1. Fabrication of the Fibers

The optical glass fiber preforms incorporated with Cu and Cu/Zn were fabricated by using the modified chemical vapor deposition (MCVD). The doping solution was prepared by dissolving a reagent grade 0.1 mole CuCl₂, 2H₂O powder (Aldrich Chem. Co. Inc., 99%) and 0.1 mole ZnCl₂ powder (High Purity Chemicals, 99.9%) with ethanol solution. Germano-silicate core layers in the silica glass tube were deposited and partially sintered and then the deposited layers were soaked with the doping solution during the MCVD process. The glass tube was again sintered, sealed to form a preform that was finally drawn into the fiber with 125 μm diameter by using the draw tower (DT) at 2150 °C. The core diameter and the cutoff wavelength of the Cu-doped germano-silicate optical glass fiber were 7.6 μm and 1.25 μm, respectively.

To investigate the effect of Zn addition in the doping solution on Cu formation of the optical glass fiber core, optical absorption and third-order optical nonlinearity, a Cu/Zn-codoped germano-silicate optical glass fiber was fabricated. The core diameter and the cutoff wavelength of the Cu/Zn-codoped germano-silicate optical glass fiber were 7.6 μm and 1.18 μm, respectively. Also, for a comparison, a germano-silicate optical glass fiber without any dopant was also fabricated. The core diameter and the cutoff wavelength of the germano-silicate optical glass fiber were 7.8 μm and 1.07 μm, respectively.

2.2. Measurements

To confirm the formation of Cu metal particles and Cu metal ions with ZnO semiconductor particles in the core of the fiber, the optical absorption spectrum of each optical fiber was measured by the conventional cut-back method where the white light source (Ando AQ 4303B) and the optical spectrum analyzer (Ando AQ 6315B) were used. Using the results of the optical absorption, the non-resonant optical nonlinear coefficient, n₂, of the Cu-doped and Cu/Zn-codoped germano-silicate optical glass fibers and the conventional germano-silicate single mode optical glass fiber without any dopant was measured by using the continuous wave self-phase modulation (SPM) method as shown in Figure 1. Details of the experiment have been reported in Refs. [19–22 and 26–28].

The effective non-resonant optical nonlinearity, γ, was estimated by using the following Eqs. (1)–(3). The non-linear phase shift ϕ_{SPM}, which is caused by self-phase modulation, and the corresponding average power of light signal P_{AVG} were measured experimentally. The ϕ_{SPM} was determined from the ratio of intensity of fundamental wavelength I₀ to the first-order harmonic signal I₁. The ratio of the spectral intensities in terms of Bessel function is given by Eq. (1).

\[
\frac{I_0}{I_1} = \frac{J_0^2(\phi_{SPM}) + J_1^2(\phi_{SPM})}{J_0^2(\phi_{SPM}) + J_1^2(\phi_{SPM})}
\]

(1)

where Jₙ is the Bessel function of nth order.

The non-resonant nonlinear refractive index coefficient, n₂, and the effective nonlinear parameter γ were estimated by Eqs. (2) and (3), respectively, i.e.,

\[
n_2 = \frac{\lambda A_{eff}}{4 \pi I_{eff}} \frac{\phi_{SPM}}{P_{AVG}} = \frac{\lambda A_{eff}}{4 \pi I_{eff}} \kappa_{nc}
\]

(2)

and

\[
\gamma = \frac{2 \pi n_2}{\lambda A_{eff}} \frac{\phi_{SPM}}{P_{AVG}} \frac{1}{2L_{eff}} = \frac{\kappa_{nc}}{2L_{eff}}
\]

(3)

where λ is the central wavelength of the two light signals (λ₁ + λ₂)/2, \kappa_{nc} is the slope coefficient from the linear curve obtained by \phi_{SPM}/P_{AVG}, and A_{eff} = (\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |F(x, y)|^2 dx dy)/(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |F(x, y)|^4 dx dy) and L_{eff} = (1 - exp(-\alpha \cdot L)/\alpha) are the effective area and the effective length of the fiber at 1550 nm, respectively.

The absorption coefficient (α) with the unit of 1/m can be readily converted to dB/m by using the following relationship:

\[
\alpha[1/m] = \frac{1}{L} \left( 10^{0.1 \alpha_{m}/10} - 10^{0.1 \alpha_{nc,m}/10} \right)
\]

(4)

Fig. 1. Experimental setup for non-resonant optical nonlinearity measurement using the cw-SPM method. TLS = tunable laser source, PC = polarization controller, BPF = band-pass filter, EDFA = erbium-doped fiber amplifier, FUT = fiber under test, VOA = variable optical attenuator, OSA = optical spectrum analyzer.
where \( \alpha_{dB} \) is the total attenuation in \( dB \) and \( \alpha_{fiber dB} \) is the background attenuation in \( dB \) (which is the same as that of the single mode fiber, 0.2 dB for 1 km length at 1550 nm).

3. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of the Cu-doped and Cu/Zn-codoped germano-silicate optical glass fibers with that of the reference fiber without dopant. In the case of the Cu-doped germano-silicate optical glass fiber, the absorption peak appeared at 445 nm due to Cu metal particles and the broad absorption band appeared from 800 nm to 1600 nm due to Cu\(^{2+}\) ions. In contrast, in the Cu/Zn-codoped germano-silicate optical glass fiber (Fig. 2), absorption peaks appeared at 435 nm and 469 nm, contributed to Cu metal particles and ZnO semiconductor particles, respectively. The reference fiber without dopants of Cu and Zn did not show any absorption peak at 435-469 nm and one absorption peak at 1380 nm was due to OH impurities.20

In the previous studies, the absorption peak of Cu metal particles in silica glass matrix was reported to be between 550 nm and 600 nm and it due to the surface plasmon resonance.35-36 However, the absorption peaks related to Cu metal particles were observed at 445 nm and 435 nm in the Cu-doped and Cu/Zn-codoped germano-silicate optical glass fibers, respectively. This blue shift of the absorption peak position of the fibers can be attributed to Cu metal particles with smaller size compared to those in the bulk silica glass.35 36

On the other hand, the broad absorption band due to Cu\(^{2+}\) ions in the glass matrix appeared in NIR region, which corresponds to three possible \( d-d \) electronic absorption transitions. According to Perez-Robles et al., the broad optical absorption band centered at 750 nm observed in Cu\(^{2+}\) xerogel was attributed to the presence of Cu\(^{2+}\) ions in the interstitial positions of the silica glass matrices.37 38

The optical absorption from 800 nm to 1.600 nm measured in the Cu-doped germano-silicate glass optical fiber can be assigned to the \( ^2E_-^2B_{1g} \) transition due to the Jahn Teller splitting of the 3d-levels of the Cu\(^{2+}\) ions in the ligand field.20 37-39 It was also observed that the concentration of water molecules and the length of the ligand field in silica matrices caused the shift in the broad optical absorption band of Cu\(^{2+}\) ions.20 Thus, the observed broad optical absorption band centered at about 1.100 nm in the Cu-doped germano-silicate optical glass fiber can be attributed to the three electronic transitions in \( d \) orbitals corresponding to \( ^2E_-^2B_{1g} \) and \( ^2A_1g^2B_{1g} \) and \( ^2B_2g^2B_{1g} \).37-39

The absorption peak at 469 nm in the Cu/Zn-codoped germano-silicate optical glass fiber was due to the strong confinement effect of ZnO semiconductor particles and the peak position was shifted relative to the exciton absorption in the ZnO-doped germano-silicate optical glass fiber reported earlier (490 nm),40 the ZnO nanorod (381 nm),41 or the thin-film of carbon encapsulated Zn-O nanosilica particles (344 nm).42 Earlier, the shift of optical absorption peak was also observed from the nano-particles embedded in the silica matrix due to quantum size effect.42-45

It is noted that the Cu/Zn-codoped germano-silicate optical glass fiber has low transmission loss at the second optical communication window of 1550 nm because of converting Cu\(^{2+}\) ions to Cu metal particles by providing reduction condition (Cu\(^{2+}\)+Zn → Cu+Zn\(^{2+}\)) due to high ionization tendency of Zn as a reduction agent during the fiber fabrication process. The intensity of the absorption at 435 nm (after baseline correction) due to Cu metal particles of the Cu/Zn-codoped germano-silicate optical glass fiber was about 0.013 cm\(^{-1}\), larger than that of the Cu-doped germano-silicate optical glass fiber (0.005 cm\(^{-1}\) at 445 nm). This stronger absorption clearly indicates that the concentration of Cu metal particles became higher in the optical fiber that was codoped with Cu and Zn due to conversion of Cu\(^{2+}\) ions to Cu metal particles by utilizing Zn as a reduction sensitizer.

The cw-SPM spectrum of the Cu/Zn-codoped germano-silicate optical glass fiber (length = 200 m) is shown in Figure 3. The zeroth-order harmonic signals with intensity \( I_0 \), appeared at 1549.81 nm and 1550.10 nm and first-order harmonic signals with intensity \( I_1 \), appeared at 1549.52 nm and 1550.39 nm. \( I_0 \) and \( I_1 \) increased linearly with the increase of the pump power. Figure 4 shows the effective phase shift (\( \varphi_{SPM}/I_{crit} \)) with the effective slope coefficient (\( k_{eff}/I_{crit} \)) of the Cu/Zn-codoped germano-silicate optical glass fiber as a function of the input pumping power of the EDFA. For a comparison, the effective phase shift (\( \varphi_{SPM}/I_{crit} \)) with the effective slope coefficient (\( k_{eff}/I_{crit} \)) of the reference fiber without dopant is also shown in the figure. As shown in Figure 4, the effective phase shift was found to increase linearly with the input pumping power. The effective slope coefficient of
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the Cu/Zn-codoped germano-silicate optical glass fibers were measured to be 0.87 W$^{-1}$·km$^{-1}$ and 1.51 W$^{-1}$·km$^{-1}$, respectively. It is noted that γ of the reference fiber was about 0.41 W$^{-1}$·km$^{-1}$. The γ of the Cu-doped and the Cu/Zn-codoped germano-silicate optical glass fibers was about 2 times and 4 times larger, respectively, than that of the reference fiber. The increase of the effective non-resonant optical nonlinearity, γ, of the Cu/Zn-codoped germano-silicate optical glass fiber, can be attributed to the enhanced nonlinear polarization due to Cu metal ions and ZnO semiconductor particles existed in the glass network. The parameters related to the optical nonlinearity of the optical fibers are listed in Table I.

It is well known that the non-resonant optical nonlinearity in glass network is due to hyper-polarizabilities of glass components such as bridging oxygens (BOs) and non-bridging oxygens (NBOs). In the case of the hyper-polarizabilities from the structure related to BOs, the nonlinear effect is very weak because BOs are strongly covalent-bonded to Si/Ge atoms and they are difficult to be distorted under applied optical electric field. On the other hand, the glass with NBOs has high optical nonlinearity because NBOs have high ionicity and they are easily distorted by applied optical electric field. The increased non-resonant optical nonlinearity of the Cu-doped germano-silicate optical glass fiber can be explained by the creation of NBOs, which was from the incorporated Cu$^{2+}$ ions in the interstitial sites of the glass structure as glass modifiers and naturally cut off the originally homogeneously-distributed and densely-connected Si-O and Ge-O bonds. In this view, the non-resonant optical nonlinearity of the Cu/Zn-codoped germano-silicate optical glass fiber should be decreased by converting Cu$^{2+}$ ions to Cu metal particles because the Zn sensitizers provide reduction condition during the fiber fabrication process. However, the non-resonant optical nonlinearity of the Cu/Zn-codoped germano-silicate optical glass fiber increased because of the creation of NBOs and defects from incorporated ZnO semiconductor particles and Cu metal ions in the optical fiber core. The large optical nonlinearity from incorporated semiconductor particles (GaAs, Ge, Si, and InAs) in the optical fiber core region is also well known due to their large nonlinear polarizability. Therefore, Zn as a reduction agent played an important role to decrease the transmission loss at the optical communication wavelength by converting

![Image](image-url)

**Fig. 3.** cw-SPM spectrum of the Cu/Zn-codoped germano-silicate optical glass fiber.

![Image](image-url)

**Fig. 4.** Variations of the nonlinear effect phase shift of the Cu-doped and Cu/Zn-codoped germano-silicate optical glass fibers with different input signal power.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Refractive index difference @1550 nm</th>
<th>Chromatic dispersion @1550 nm</th>
<th>Absorption coefficient @1550 nm</th>
<th>Effective length</th>
<th>Effective area</th>
<th>Effective refractive index</th>
<th>Nonlinear refractive index</th>
<th>Effective nonlinear coefficient</th>
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<tr>
<td>Symbol</td>
<td>D</td>
<td>α</td>
<td>l_{eff}</td>
<td>A_{eff}</td>
<td>κ_{eff}/l_{eff}</td>
<td>n_{2}</td>
<td>γ</td>
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<td>μm$^2$</td>
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<td>rad/m·mW</td>
<td>m$^{-1}$·W</td>
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<tr>
<td>Ref. fiber</td>
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<td>1.67 × 10$^{-4}$</td>
<td>170.03</td>
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<td>0.4117</td>
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<td>0.8673</td>
</tr>
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<td>Cu/Zn-codoped fiber</td>
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<td>1.59 × 10$^{-4}$</td>
<td>60.27</td>
<td>103</td>
<td>2.99 × 10$^{-4}$</td>
<td>3.8362 × 10$^{-28}$</td>
<td>1.5097</td>
</tr>
</tbody>
</table>

Table I. Non-resonant nonlinear optical parameters of the fibers.
Cu$^{2+}$ ions to Cu metal particles and to the enhanced nonlinear polarization due to Cu metal ions and ZnO semiconductor particles existed in the glass network, which makes it suitable for high-speed-high-capacity optical communication systems.

4. CONCLUSION

We fabricated the Cu/Zn-codoped germano-silicate optical glass fiber for nonlinear optical applications by solution doping techniques in the MCVD process. The addition of Zn sensitizer was found to be effective to convert Cu metal ions to Cu metal particles by providing reduction condition during the MCVD process and to increase the non-resonant third-order optical nonlinearity. The absorption peak appeared at 445 nm and the broad absorption band from 800 nm to 1600 nm in the Cu-doped germano-silicate optical glass fiber were found due to surface plasmon resonance form Cu metal particles and Cu$^{2+}$ ions, respectively. And the absorption peak appeared at 435 nm and 469 nm in the Cu/Zn-codoped germano-silicate optical glass fiber was found due to Cu metal particles and ZnO semiconductor particles, respectively. Also, the Cu/Zn-codoped germano-silicate optical glass fiber has low transmission loss at the second optical communication window of 1550 nm because the Cu/Zn-codoped germano-silicate optical glass fiber where converting Cu$^{2+}$ ions to Cu metal particles.

The non-resonant nonlinear refractive index coefficient, $n_2$, of the Cu-doped and Cu/Zn-codoped germano-silicate optical glass fibers was estimated to be $2.52 \times 10^{-20}$ m$^2$/W and $3.84 \times 10^{-20}$ m$^2$/W, respectively. The effective nonlinear parameter, $\gamma$, of the Cu-doped and Cu/Zn-codoped germano-silicate optical glass fibers was found to be 0.87 W$^{-1}$km$^{-1}$ and 1.51 W$^{-1}$km$^{-1}$, which was about 2 and 4 times larger than that of the reference fiber without dopant. The increase of the effective non-resonant optical nonlinearity, $\gamma$, of the Cu/Zn-codoped germano-silicate optical glass fiber, can be attributed to the enhanced nonlinear polarization due to incorporated ZnO semiconductor particles and Cu metal ions in the glass network.

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References and Notes


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