







## 2. Experimental

A preform of a germano-silicate glass optical fiber was manufactured by using the MCVD process. To increase the refractive index of the preform core for guiding a light, 0.03 mole  $\text{GeO}_2$  was added to main constituent of  $\text{SiO}_2$ . After deposition of the core layers in the silica glass tube, a doping solution containing PbTe SQDs was sprayed into the tube at  $1000^\circ\text{C}$  by using the atomizer (Model 9302, TSI Incorporated). The doping solution containing PbTe SQDs was prepared by dissolving reagent grade PbO and Te powders in nitric acid solution (0.03 mole of PbTe). Then the tube was dried, sintered and sealed to obtain a fiber preform. The fiber preform was drawn into a fiber using the draw tower at  $2150^\circ\text{C}$ . The core diameter and the cutoff wavelength of the PbTe doped germano-silicate glass optical fiber were  $9.6\ \mu\text{m}$  and  $1.2\ \mu\text{m}$ , respectively. Another PbTe doped germano-silicate glass optical fiber by using the soaking process was also fabricated having the core diameter of  $6.3\ \mu\text{m}$  and the cutoff wavelength of  $1.0\ \mu\text{m}$ . Also, for a comparison, the germane-silicate optical fiber without PbTe was also fabricated. The core diameter and the cutoff wavelength of the germano-silicate optical fiber were  $9.0\ \mu\text{m}$  and  $1.1\ \mu\text{m}$ , respectively.

To confirm formation of PbTe SQDs in the core of fiber preforms, core portions of the preforms were examined by the X-ray Diffractometer (XRD) and transmission electron microscopy (TEM, FEI Tecnai G2 F30 S-TWIN) measurements. Optical absorption spectra of germano-silicate glass optical fibers incorporated with PbTe SQDs were measured by the cut-back method where the white light source (Ando AQ 4303B) was used for launching the broadband light into the fiber and the OSA (Ando AQ 6315B) for the output spectrum.

Using the data of the optical absorption spectrum, we chose the wavelength of pump LD to measure resonant optical nonlinearity of the PbTe doped optical fibers. To compare the resonant nonlinearity of the PbTe doped germano-silicate glass optical fiber, the resonant nonlinearity of germane-silicate optical fiber (without PbTe SQDs) was also measured. The nonlinear refractive index of fibers was estimated by measuring the peak shift of the interference fringes formed due to the long period grating (LPG) pair upon pumping with the laser diode (LD). The LPG pair was fabricated on a conventional single mode fiber (SMF) by using an amplitude mask of  $450\ \mu\text{m}$  period to form interference fringes near  $1530\ \text{nm}$ . Prior to inscribe the grating, the SMF was hydrogen loaded at  $50^\circ\text{C}$  under the pressure of  $10\ \text{MPa}$  for a week. The gratings were inscribed on the bare fiber with the KrF excimer laser ( $248\ \text{nm}$ ) and then the fiber was annealed at  $150^\circ\text{C}$  for 24 h. The PbTe doped fiber was spliced between a pair of the LPG as shown in Fig. 1. The details for the measurement are described elsewhere [30,54,55]. Figure 1 shows the schematic diagram of the optical nonlinearity measurement setup. The total length,  $L$ , between the LPG pair including the PbTe doped germano-silicate glass optical fiber was  $37.65\ \text{cm}$ , whereas the length,  $L_1$ , of the PbTe doped germano-silicate glass optical fiber was  $29.25\ \text{cm}$ . Two wavelength division multiplexers (WDM) ( $980\ \text{nm}/1550\ \text{nm}$ ) were used to multiplex and demultiplex the pump beam at  $976.4\ \text{nm}$  and the signal light near  $1550\ \text{nm}$ , respectively. The interference fringes in the region of  $1500\sim 1550\ \text{nm}$  were monitored to determine the nonlinear index.

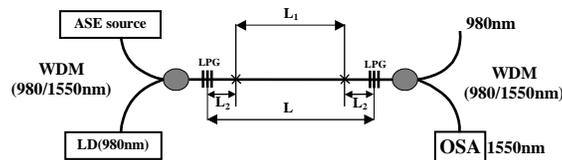


Fig. 1. Schematic diagram of the setup for nonlinearity measurement of the PbTe SQDs doped germano-silicate glass optical fiber by use of the LPG pair.

## 3. Results and discussion

Comparison of the X-ray diffraction patterns of the PbTe SQDs doped preforms prepared by the atomization process and the conventional soaking process and the preform having no PbTe

quantum dots is shown in Fig. 2. The fiber preforms doped with PbTe clearly showed a diffraction peak at  $2\theta = 21.6^\circ$ , regardless of the doping process. Note that for the preform without dopants, no diffraction peak but diffused background was found. These XRD results clearly indicate that PbTe particles were formed in the core of the PbTe-doped preforms. A rather broad feature of the diffraction peak of the preforms doped with PbTe was due to the size effect of PbTe SQDs. It can be seen in Fig. 2 that the peak intensity in the XRD pattern for the preform doped with PbTe using the atomization process was slightly larger than that by the soaking process, indicating the higher concentration of the PbTe in the preform by the atomization process. The atomization process seems to bring about higher dopant concentration and easier operation than the soaking process. The existence and size distribution of the PbTe SQDs were verified again by TEM morphology of the fiber preforms as shown in Fig. 3. The average diameter of PbTe SQDs was 4.61 nm (3.54 nm ~6.03 nm) and 5.49 nm (4.02 nm ~6.03 nm) in the fiber preforms made by atomization process and soaking process, respectively. The TEM photograph clearly shows the morphology of the SQDs, which is crystalline, to be roughly spherical and homogeneous without agglomeration. From the TEM morphology of the PbTe doped fiber preforms, the formation of PbTe SQDs in the core was also confirmed and both the concentration and the size distribution of PbTe SQDs were found to increase and widen by atomization process compared to those by the soaking process, because the atomization process was done by spraying very fine droplets of the doping solution into the fiber preform.

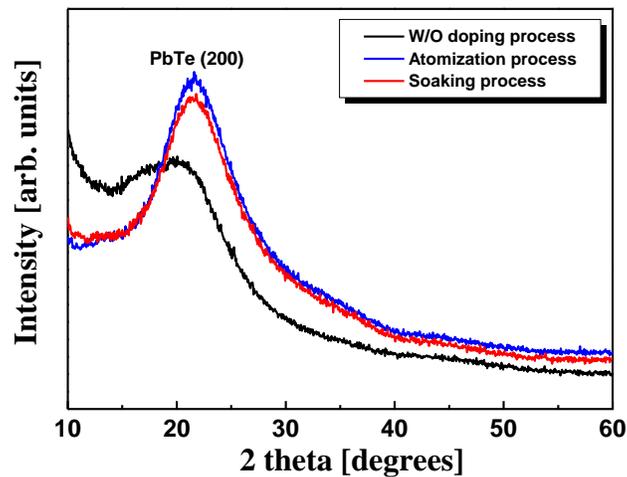


Fig. 2. Effect of the doping process on the XRD patterns of the PbTe SQDs doped germano-silicate glass optical fiber preforms.

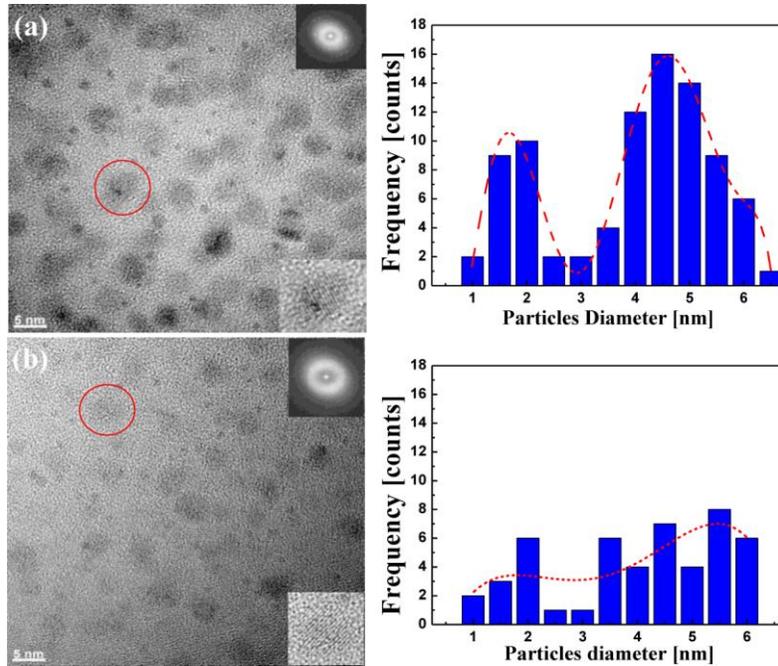


Fig. 3. TEM image and size distribution of the PbTe SQRs in the core of the fiber preforms prepared by (a) atomization process and (b) soaking process. (0.03 mole).

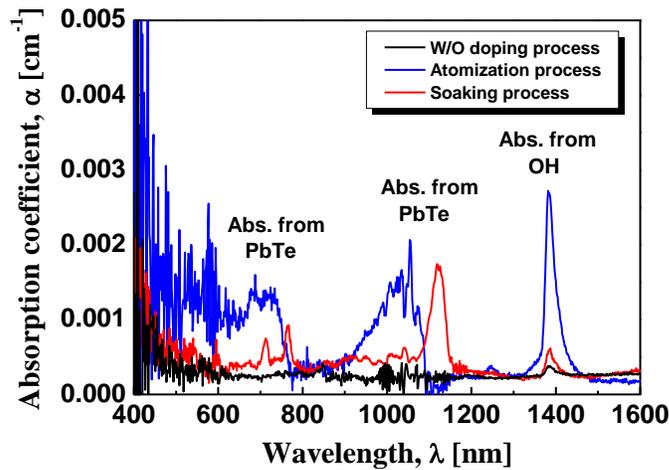


Fig. 4. Absorption spectra of the PbTe SQRs doped germano-silicate glass optical fibers prepared by atomization doping process and soaking process.

The wide size distribution and the high concentration of PbTe SQRs in the germano-silicate glass optical fibers were also verified by the optical absorption spectra of the fibers as shown in Fig. 4. The absorption bands at 687 nm and 1055 nm of the fiber made by adopting the atomization process and the absorption bands at 712 nm, 775 nm, and 1120 nm of the fiber by the soaking process (Fig. 4) are attributed to quantum confinement of PbTe SQRs in the fiber core [28–33]. The absorption bands around 700 nm and 1100 nm of the fiber samples showed two distinguishable excitonic peaks and these peaks of the PbTe SQRs doped germano-silicate glass optical fibers were well matched with the two groups of different sized

PbTe SQDs as shown in Fig. 3. The difference in the peak wavelengths of the absorption bands of the two fibers was attributed to the size effect of PbTe SQDs embedded in glass matrix, smaller the average size, shorter the peak wavelength [28,32–34]. The observed bimodal distribution of PbTe SQDs in the core region of the fabricated fiber preforms and fibers may be due to the non-uniform distribution of the GeO<sub>2</sub> in the core. The fiber preforms processing parameters such as the soot deposition temperature, which is related the porosity of the glass, and the solution drying temperature may influence the bimodal size distribution of PbTe SQDs. The formation kinetics of PbTe SQDs in germane-silicate glass system may be different resulting in different size of PbTe SQDs due to different GeO<sub>2</sub> concentration [56]. Since the atomization process allowed the porous deposition layers to contact with the fine droplets of the doping solution, an effective area of the adsorption was expected to increase and therefore the incorporation of the PbTe SQDs becomes extended as compared to the soaking process where wetting of the porous layers by doping solution occurred due to adhesion.

It can also be seen that the absorption band shape in both the fibers was different. The absorption band of the fiber by the atomization process was broader, indicating wider size distribution of PbTe SQDs, than that by the soaking process. Because the atomization process was done by spraying very fine droplets of the doping solution into the preform tube during the MCVD process, it may have resulted in the variation in the size of PbTe SQDs, depending on the size of the droplet, which gives rise to the broad absorption band. The absorption peak at 1380 nm was because of the OH impurities. It is interesting to note that the PbTe SQDs, which were embedded in the core of preform, were still preserved in the core of the fiber even after drawing the fiber from preform at a high temperature of about 2150°C.

As stated earlier, to find the nonlinear refractive index,  $n_2$ , of the fibers, the peak wavelength shift of the interference fringes formed due to the LPG pair and 976.4 nm pump were measured and the results are shown in Fig. 5 for the PbTe SQDs doped germano-silicate glass optical fibers. While the fringes were found to shift toward the longer-wavelength side with the increase of pump power in the case of the fiber that used the atomization process, no appreciable fringe shift was found in the fiber that used the soaking process apparently because of the absence of absorption peak of PbTe SQDs in that fiber at 976.4 nm. Therefore, it is evident that because of a resonant type of the high nonlinear optical fiber, the wavelength shift in the fiber that used atomization process can be attributed to the nonlinear optical property of the PbTe SQD doped germano-silicate glass optical fiber at 976.4 nm.

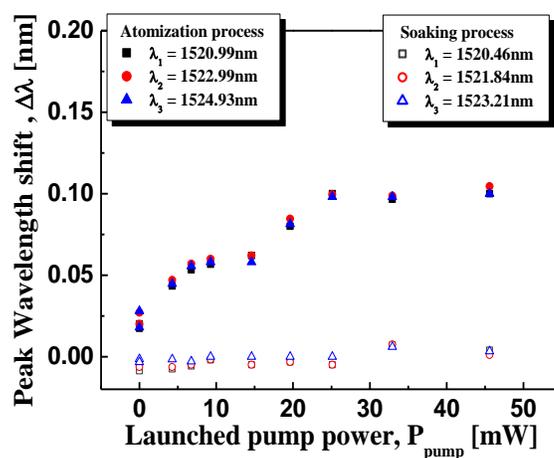


Fig. 5. Wavelength shift of the interference fringes near 1523nm of the PbTe SQDs doped germano-silicate glass optical fibers by using the atomization process and the soaking process upon pumping with the LD at 976.4 nm.

The nonlinear refractive index,  $n_2$ , of the PbTe SQDs doped germano-silicate glass optical fibers was estimated from the results shown in Fig. 5 [35,54]. Figure 6 shows the estimation of nonlinear refractive index,  $n_2$ , of the PbTe SQDs doped germano-silicate glass optical fiber by using the atomization process upon pumping with the LD at 976.4 nm. The  $n_2$  of the fiber that utilized the atomization process was found to be from  $3.9 \times 10^{-16}$  to  $0.8 \times 10^{-16}$  m<sup>2</sup>/W at the pump power from 4.3 mW to 45.6 mW. The nonlinearity of the PbTe doped germano-silicate glass optical fiber by the atomization process may be due to a population inversion of PbTe ions by the optical pump at 976.4 nm. On the other hand, the  $n_2$  of the fiber made by the soaking process and the reference fiber was about  $5.1 \times 10^{-18}$  m<sup>2</sup>/W and  $8.7 \times 10^{-19}$  m<sup>2</sup>/W at the pump power 45.6 mW, respectively. The major parameters related to the optical nonlinearity of the PbTe SQDs doped germano-silicate glass optical fibers and the reference fiber are listed in Table 1.

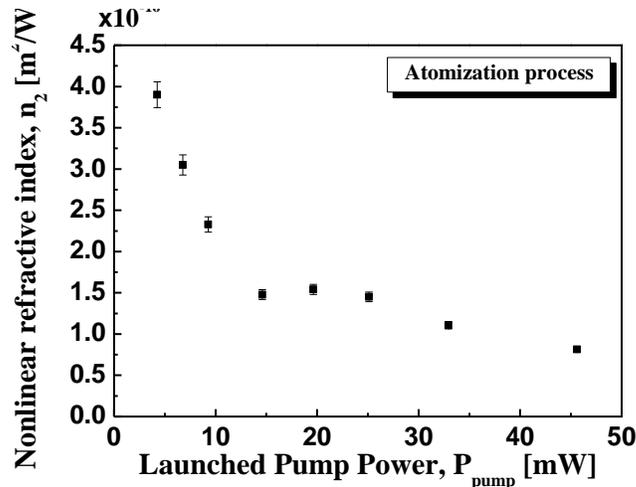


Fig. 6. Estimation of nonlinear refractive index,  $n_2$ , of the PbTe SQDs doped fiber by using the atomization process upon pumping with the LD at 976.4 nm.

Table 1. Optical parameters of the fibers incorporated with PbTe SQDs

Doping process	$\Delta n$	$\lambda_c$	$A_{\text{eff}}$	S	$\Delta\lambda$	$P_{\text{pump}}$	$n_2$
Unit	%	nm	$\mu\text{m}^2$	nm	nm	mW	$\times 10^{-17}\text{m}^2/\text{W}$
W/O doping process	0.50	1.11	15.9	4.14	0.00150	45.6	0.09
Atomization process	0.31	1.19	14.7	3.94	0.10000	45.6	8.15
Soaking process	0.50	0.99	10.8	2.76	0.00333	45.6	0.51

$\Delta n$  = the refractive index difference between the core and the cladding of the fiber

$\lambda_c$  = the cut-off wavelength of the fiber

$A_{\text{eff}}$  = the effective area around 1550nm

S = the fringe spacing

$\Delta\lambda$  = the wavelength shift of the LPG fringes

#### 4. Conclusion

We proposed a new doping process, so-called atomization process, to incorporate PbTe SQDs in the core of the fiber for nonlinear optical application. The atomization doping process was found to be simple in operation and more effective to increase of the dopant concentration than the soaking process.

The X-ray diffraction peaks of the PbTe SQDs in the core region of the PbTe SQDs doped optical fiber preforms appeared at  $2\theta = 21.6^\circ$ , regardless of the doping process. The average diameter of PbTe SQDs was around 4.61 nm (size distribution: 3.54 nm to 6.03 nm) and 5.49 nm (size distribution: 4.02 nm to 6.03 nm) in the PbTe SQDs doped fiber preforms made

by atomization process and soaking process, respectively. The size distribution of PbTe SQDs in the PbTe SQDs doped fiber preforms was found to be bimodal and the concentration of PbTe SQDs in the fibers was also verified by the optical absorption spectra of the fibers. The absorption bands at 687 nm and 1055 nm of the fiber made by the atomization process and those at 712 nm, 775 nm and 1120 nm of the fiber by the soaking process were attributed to quantum confinement of PbTe SQDs in the fiber core. The absorption bands were shifted according to the size effect of the compound PbTe SQDs in glass matrix by the doping process in MCVD process.

The nonlinear refractive index,  $n_2$ , was estimated by measuring the wavelength shift of the interference fringes obtained from the PbTe SQDs doped germano-silicate glass optical fiber spliced with a LPG pair upon pumping with laser diode at 976.4 nm. The nonlinear refractive index of the PbTe SQDs doped germano-silicate glass optical fiber made by use of the atomization process was found to decrease with the increase of the launched pump power and it was  $\sim 1.5 \times 10^{-16} \text{ m}^2/\text{W}$  near 1523 nm at the pump powers of 14.6 ~25.1 mW.

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