PbTe Quantum Dots in Tellurite Glass Microstructured Optical Fiber

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Abstract

PbTe doped tellurite glass photonic optical fiber for non linear application were developed using rod in tube method in a draw tower. We follow the growth kinetics of the quantum dots in the optical fiber by High Resolution Transmission Electron Microscopy giving some results related with the growth kinetic of the same in function of time so much for optical fiber as for the glass bulk. Absorption peak near 1500 nm as observed and it was attributed the optical resonance due PbTe quantum dots in the core fiber.

I-Introduction

Semiconductor quantum dots (QDs)-doped glasses have attracted much attention because they exhibit large optical nonlinearities as well as fast response times (less than 1 ps) potentially useful for ultra fast all optical devices. Tsunetomo et al. [1] have demonstrated a 250 Gbit/s Fabry-Perot optical device with CdTe QDs embedded in a silica glass host. An Optical Fiber device, however, would be better suited for optical telecommunications purposes. These fiber devices can become real if a PbX core doped and undoped clad can be made. PbE (E = S, Se or Te) QDs show the absorption peaks in the optical communication window [2] making them a natural material candidate for photonic devices. The first report on this area [2] using PbS nanostructures in borosilicate glasses showed absorption in the 1000 to 2000 nm region. This report was soon followed by the fabrication of PbSe [3] in phosphate glasses and PbTe in borosilicate glasses [4,5]. Although all these glasses showed the optical band gap in the wavelength region used for optical communications, 1300 and 1500 nm, they all present low QD concentration due to the semiconductor low solubility in the vitreous system. The high QD solubility of tellurite glass, order of magnitude larger than other glass systems, like borosilicate glasses, made it attractive for the glass matrix host. The price to pay for high QD's concentration is a larger dispersion of the QD's size. Our results to tellurite glasses, however, show that it is worth doing this [6]. First, because there is almost no broadening for diluted systems (volume fraction up to 0.01). Second, because even for volume fractions of 0.3 the dispersion is less than 1.5 times larger than the dispersion of diluted systems. In the past we showed that PbTe QD doped core/undoped clad optical fiber could be produced with tellurite glass. The difficult to make a conventional core/clad optical fiber was the thermo physical matching of the core and clad glass together with the desirable refractive index mismatch for light guiding. We only succeed after trying with a great number of glass compositions. Photonic Crystal Fibers (PCF), however, presents none of these problems because it uses the same glass, automatically matching the thermo physical properties, while the light guiding is provided by the hollow parts and geometry. For these reasons we decided to produce a PbTe QD doped tellurite glass PCF. The purpose of this work is to show tellurite glasses photonic optical fiber doped with PbTe quantum dots. We used High Resolution Transmission Electron Microscopy (HRTEM) and optical absorption spectroscopy to characterize the QD's size distribution, concentration and optical band gap.

II-Experimental

The fiber core was made with **35TeO_2 - (10 to 15)ZnO - (15 to 35)CdO - (10 to 25)20B_2O_3 - (20 to 30)BaO - 20PbO (wt%)** doped glasses prepared by mixing tellurium oxide (TeO_2, 99.9995%), zinc oxide (ZnO, 99.999%), barium oxide (Ba_2O_3, 99.995%), lead oxide (PbO, 99.999%), cadmium oxide (CdO, 99.999%) and boron oxide (B_2O_3 99.999%) doped up to 15wt% PbTe (PbO + Te metallic). This raw material was melted and homogenized at 950 ºC in a platinum crucible during 180 minutes and had been sucked by a quartz pipe to produce doped bars. This process has been very fast to avoid any initial QD growth and obtain clear glass sheets. The time for suction was around of 0,5s. These bars have a length of 150 mm for 8 mm of diameter. A thermal annealing in a controlled atmosphere of oxygen at 380°C, very close to the glass transition temperature T_g, for 5 hours was done to diminish stresses. The QD nucleation happened at 400°C for another 8 hours and the QD growth was done at 450°C. Identical samples in the form of 1 mm thick laminas were

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thermally annealed at 450°C to grow the QD and removed from the furnace after 25, 27, 29, 31, 33, 35, 38 and 42 hours. From the 1mm thick laminas spectra obtained we choose the 31 hours at 450°C growth time for the whole core bar. After the growth the quantum dot bar was drawn down to 1 mm in a Heathway drawing tower, as showed in figure 1a. The glass tubes used the same material without the PbTe doping. It was melted at 950°C for 4 hours and then sucked in a quartz tube. This tube was then placed in a system with rotation speed and temperature control to control the tube thickness and eliminate any bubbles. The capillaries were obtained by drawing this 15 mm tube down to 1mm after removal from the quartz tube and cut in 20 cm long pieces, as shown in figure 1b.

1a) 1b)

Figure 1: (a) Bars and micro doped bars with PbTe quantum dots and (b) Tubes and micro tubes of telluride glass to produce photonic optical fiber. The difference of colors presented in the illustration of the tubes is due to the tubes that involve the core they also contain PbTe.

The capillaries and the core bar were stacked inside a 12mm diameter tellurite glass tube as shown in figure 2 (left). One end of the 12 mm tube was strangled to avoid fall of the capillaries and core bar. This PCF perform was finally drawn at 750°C with 2 m/min draw speed under vacuum to avoid the collapse of the tubes. Figure 2 (right) show the photonic optical fiber with core doped with PbTe quantum dots of a preform with 96 capillaries. The main problem with these fibers is the QD crystallization. The irregularities seen in the picture are due to high drawing temperature used necessary to avoid this QD crystallization. We are in the process of changing the glass host to increase the thermal stability range to drawn these fibers.

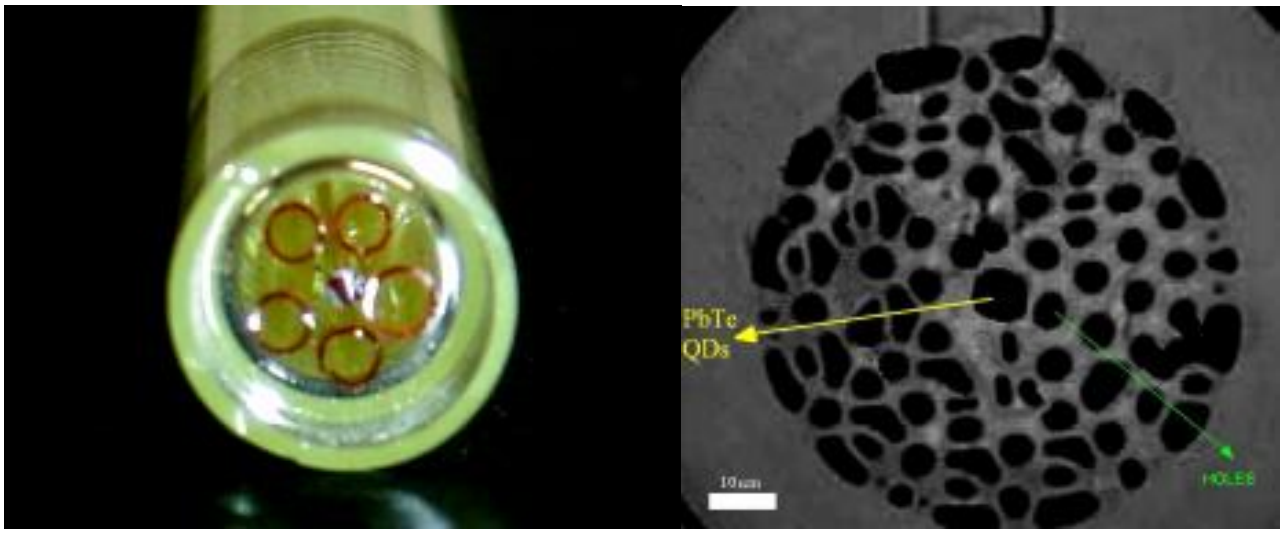

Figure 2: Exemply of preform of the telluride glass photonic optical fiber with PbTe quantum dots with 5 tubes and a clad bar (left) and PCF drawing with 60 tubes and annealed to 450°C.

Each 1 mm slice annealed for 25 to 42 hours at 450°C was characterized by HRTEM and optical absorption spectroscopy. The sample preparation for HRTEM consists of dimpling and ion milling and then crunched and diluted in

isopropanolic alcohol. This solution was dripped into a NaCl crystal and catched with a cooper net as a free standing quantum dot glass/carbon film after NaCl dissolution in water. A piece of the final optical fiber was triturated to obtain smaller than 10 microns grains for the HRTEM measurements of the QDs inside the optical fiber. This film was analyzed in a JEOL 300 kV TEM operating at 300 kV. We checked the presence of Te and Pb by Electron Diffraction X-rays (EDX) and perform a Fourier transform on the digital micrographic photos to obtain the lattice parameters using the Digital Micrograph Software. Two lenses were used to focus the light of a Fourier Transform Spectrometer into the fiber and out of the fiber back to spectrometer detector. We used a fiber with the core not annealed, without quantum dots therefore, as the background spectrum.

III-Results and Discussion

High Resolution Transmission Electronic Microscopy (HRTEM) shows the presence of the quantum dots inside the fiber core as shown figure 3. The joined particles seen in the picture are similar to the results found for tellurite glass samples in bulk (6). For the preform treated for 31 hours (the same core of the doped optical fiber with PbTe of our previous paper [7]), the result of a 10 mm long fiber piece is shown in Figure 4. The reduced size of the fiber is due to the great absorption of the quantum dots. The absorption peak around 1300 nm is well inside the optical communications spectral window.

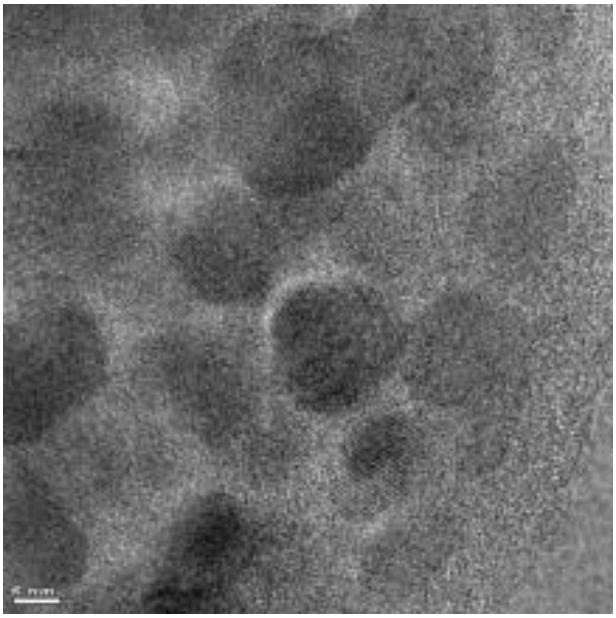

Figure 3: HRTEM of the doped tellurite glass fiber with PbTe. Annealing for 31 hours

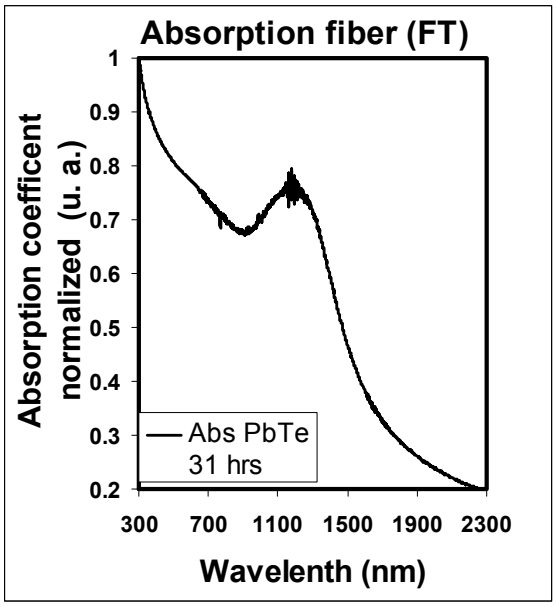

Figure 4: absorption specter of the doped optic fiber with PbTe.

IV-The growth kinetics for quantum dots in photonic crystal optical fiber.

The growth kinetics was followed by measuring about 100 QD's radii for each sample from 27 to 42 hours treatment time. Figure 5 shows the average radius as a function of the cubic root of the treatment time to tellurite glass doped with PbTe quantum dots and the doped optical fiber with same semiconductor.

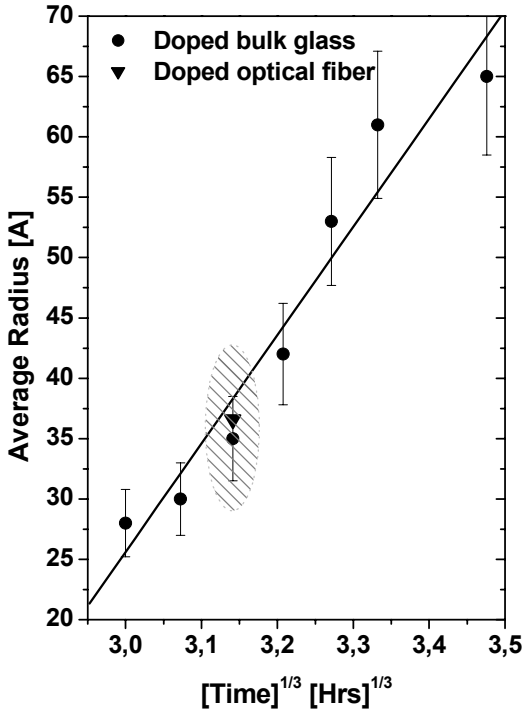

Figure 5. Average radius as a function of cubic root of time for QD's growth at 450°C.

The straight line shows that the experimental data fits well with a $t^{1/3}$ growth law typical of Ostwald ripening [8,9]. For very small volume fraction Q [6] the QD's size distribution follows the Lifshitz-Slyozov distribution [10]. But for higher Q, the gradient concentration field of each QD interacts with the other and the distribution becomes broader, although the $R = b\ t^{1/3}$ behavior do not change. It is possible to extract the Q value from the size dispersion measurements by following the steps: (1) constructing a normalized distribution from the frequency for each radius. To do this we multiply the radius by a constant a = area/average radius and the frequency by a constant b = average radius/squared area. This manipulation makes, both, the average normalized radius and the area under the probability density, always equal to 1. (2) Obtain the new distribution as a function of the volume fraction Q. Among the several reports about higher fractions of solute particles, Enamoto [8] and Marqusee [9] presented the most elegant treatments. Enomoto's recipe for this is the following: given some Q, the second (m_2) and third (m_3) moments of the distribution values, use his equation number 2.4 to calculate the critical radius. Using the distribution given by equation 2.7, recalculate the m_2 and m_3 values and let the system converge after a number of iterations. At the end, normalize the final distribution by the step (1) of the recipe above. (3) Adjust the Q value for the minimum squared deviation. This can be done in an Excel worksheet. Figure 6 and 7 show the normalized distribution for the 31 hour sample bulk and optical fiber, square points, for the minimum square deviation Q = 0.54 to glass bulk and Q = 0,51 to optical fiber value, thick line, and the LS distribution.

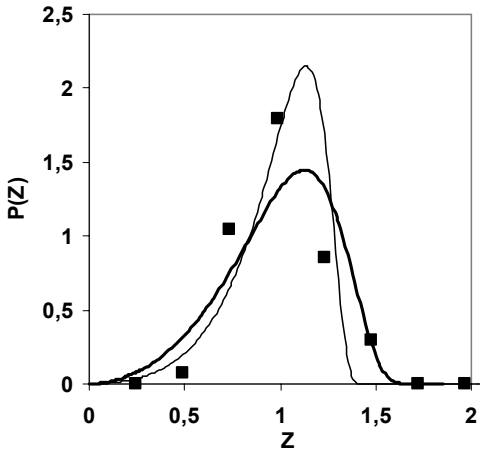

Figure 6. Normalized size distribution for the experimental data (squares) in tellurite glass bulk, Q = 0.54 volume fraction (thick line) and LS distribution (thin line).

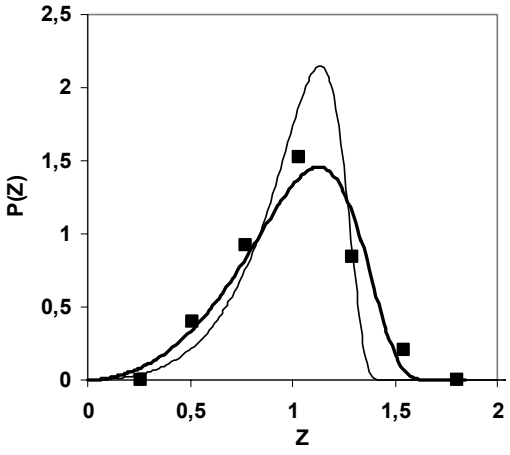

Figure 7. Normalized size distribution for the experimental data (squares) in tellurite glass optical fiber, Q = 0.51 volume fraction (thick line) and LS distribution (thin line).

These results showed how the very high QD's concentration affects the growth kinetics and the size distribution the same way in the bulk glass and in the optical fiber. This probably means that the 720°C thermal cycles for 20 minutes of the fiber drawing process was too fast to change the QD growth kinectics. The whole picture is consistent with a growth affected by the high volume fraction. This explains why the QD's size distribution is larger in this glass compared with the borosilicate glass ones, in the low solubility regimen. Our earlier studies of PbTe QD's in borosilicate glass using SAXS and HRTEM showed that the size and size distribution measured by SAXS coincides with the ones measured by HRTEM and exhibit the same $R = b\, t^{(1/3)}$ dynamics but with much lower broadening.

V-Conclusion

We showed that is possible to produce photonic crystal optical fiber with the core doped with PbTe quantum dots. We also showed that these PCF maintain the same QD growth kinetics of the bulk vitreous material, meaning that the drawing process does not have an effect on the growth kinetics.

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