Tellurite Glass Optical fiber doped with PbTe Quantum Dots

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ABSTRACT

We produced a PbTe quantum dot core doped optical fiber with tellurite glasses intended to be used in highly nonlinear ultrafast optical devices capable to operate at the optical communication window at 1300 and 1500 nm wavelength region. Attenuation peaks of the optical fiber depends on the heat treatment time as expected for dots growth and covered the whole mid infrared region near 1500 nm. The optical fiber preform was made with the rod-in-tube method and the fiber was produced with a 4 m high Heatway drawing tower. The optical fiber core can be heavily doped because tellurite glasses solubility for PbTe quantum dots is order of magnitude higher than borosilicate and phosphate glasses, for example. In order to match all the requirements for core-clad optical fibers we studied undoped and doped tellurite glasses optical and thermophysical properties as a function of the glass composition. We also followed the growth kinetics of the quantum dots by High Resolution Transmission Electron Microscopy in the bulk glass matrix and the optical fiber.

1 –INTRODUCTION

Recent efforts to develop and study the properties of IV-VI quantum dots (QD), specially PbX (X=S, Se and Te), in glasses are mainly because their optical gaps can be controlled to fall right in the 1300 and 1500 nm spectral windows used in telecommunication[1]. Their small bulk band gap, of order of 300 meV, small effective masses and, consequently, large Bohr radius, gives rise to strong quantum confinement, of order of 500 meV, which brings the optical band gap to the desired 800 meV region[2]. Quantum dots tend to exhibit large and fast response optical nonlinearities that could be used for optical switching if the material absorption lies in the right wavelength region. The first report on this area, using PbS nanostructures in borosilicate glasses, showed absorption in the 1000 to 2000 nm region[3] and was soon followed by the fabrication of PbSe[4] in phosphate glasses and PbTe in borosilicate glasses[5]. All these works show the desired mid infrared peaks but in bulk glasses, not suitable for a real optical device. Real optical devices may be produced with quantum dots doped optical fibers, as shown is this work, planar waveguides or Fabry-Perot multilayer structures[6].

Tellurite glasses for the QD matrix host presents several advantages in terms of both, optical fiber production and quantum dots quality. First because its thermo physical properties are well suited for optical fiber drawing. Second because its solubility for PbX QDs is orders of magnitude higher than in other glass systems, like borosilicate glasses, solving the problem of low QD concentration that existed before[7,8]. Third its low softening point temperature around 300^{o}C is specially suited for good quality quantum dots growth that requires annealing at the 300-500^{o}C range. Fourth, this is a multicomponent glass, we used TeO_2-ZnO-CdO-B_2O_3-BaO-PbO, that provides enough freedom to the match the core-clad optical and thermo physical requirements for optical fibers just by playing with the glass composition. This report shows the first, as far as we know, tellurite glass PbTe QD doped core/undoped clad optical fiber, although there was an earlier report on PbTe silica glass optical fiber made by Modified Chemical Vapour Deposition (MCVD)[9,10]. Silica glasses optical fibers require MCVD and drawing temperatures too high to obtain good quality quantum dots, that tend to evaporate and present very low QD concentration of highly size dispersed QDs.

There is a restrict set of condition that must be satisfied by the materials in order to produce core/clad optical fibers. The first condition is that both, core and clad, glasses must have the working temperature T_w, where their viscosity is around $10^{5.5}$ poise, ideal for drawing, in the Thermal Stability Range (TSR = T_x -T_g), that is, above the vitreous transition temperature T_g and below the onset of crystallization temperature T_x, otherwise or its impossible to draw the fiber below T_g, or the fiber becomes useless due to the microcrystals light scattering and terrible mechanical properties. Usually the TSR must be of order or larger than 100 K. There are also core/clad mismatching limitations on the thermal expansion coefficients and, of course, the core refractive index must be controlled to be slightly higher than the clad one to obtain single mode optical fibers. The only way we could meet

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all these hard requirements was by measuring the optical and thermo physical characteristics of several tellurite glasses compositions, changing the contents of TeO_2-ZnO-CdO-B_2O_3-BaO-PbO glass family two by two. After discarding the composition that presented glass crystallyzation we ended up with 25 compositions to study. Then we succeed to find at least two compositions, one for the core and the other for the clad, ideal to produce the optical fibers and the PbTe QD.

2 – EXPERIMENTAL, RESULTS AND DISCUSSIONS

Glass preparation: for the undoped tellurite glasses we used the compositions (35-55) TeO_2 - (0-15) ZnO - (0-20) CdO - (0-20) B_2O_3 - (5-35) BaO – (0-35) PbO (wt%) by mixing tellurium oxide (TeO_2, 99.99%), zinc oxide (ZnO, 99.99%), barium oxide (Ba_2O_3, 99.99%), lead oxide (PbO, 99.99%), cadmium oxide (CdO, 99.99%) and boron oxide (B_2O_3 99.99%). These glasses were melted at 850°C in platinum crucible during 8 hours in an O_2 rich atmosphere and quenched. Samples of the several compositions were used to perform the optical and thermo physical characterizations. For the doped glasses we looked for the PbO rich compositions and added to them an excess of 15wt% PbTe (PbO + Te metallic). This raw material was then melted and homogenized at 950 ºC in a platinum crucible during 180 minutes in a CO_2 rich atmosphere and quenched. Samples of these bulk glasses were separated to perform QD growth kinetics studies as well as their optical and thermo physical properties. Both, doped and undoped glasses were thermal annealed at 380°C, very close to T_g, for 5 hours to diminish stresses. The QD nucleation happened at 400 °C for 8 hours followed by the QD growth at 450°C for 25, 27, 29, 31, 33, 35, 38 and 42 hours.

Preform preparation: after choosing the compositions for the clad and core glasses it was necessary to obtain a rod and a tube out of them. To do this the quenching was suppressed and the melt was sucked inside a quartz pipe. High sucking velocity produced the tube while low velocity produced the rod. The time for the rod suction was around of 0,5s to avoid uncontrolled QD nucleation and growth at this stage. Figure 1 shows the 150 mm long undoped tube with 1 mm internal diameter and 150 mm long doped rod with 8 mm external diameter after heat treatment for QD growth. The QD doped rod was drawn in a 4 m high Heatway drawing tower until its external diameter could fit the 1 mm internal tube diameter to form the rod-in-tube preform. Figure 2 shows the optical fiber obtained after the preform drawing with 125 μm outer diameter and 12 μm core diameter. The core, therefore, was drawn twice at 450°C but with time much smaller than the QD growth time in such a way that no QD was formed in these processes. The core QD growth happened at a posterior controlled heat treatment of the fiber already drawn again at 400 °C for QD nucleation and 450°C for QD growth.

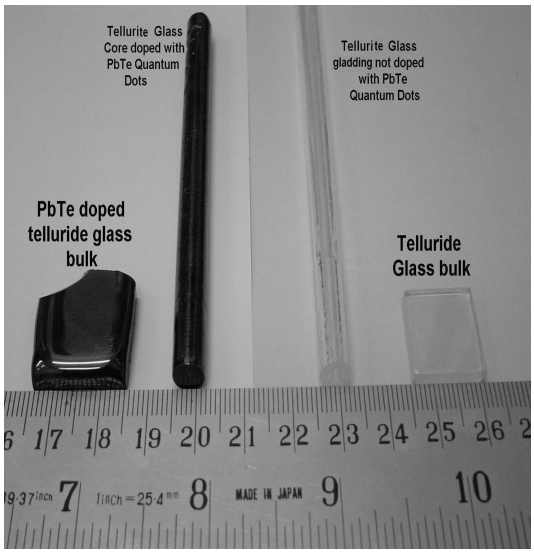

Figure 1: Left: black sample and rod of QD doped glass. Right: transparent tube and sample of undoped glass.

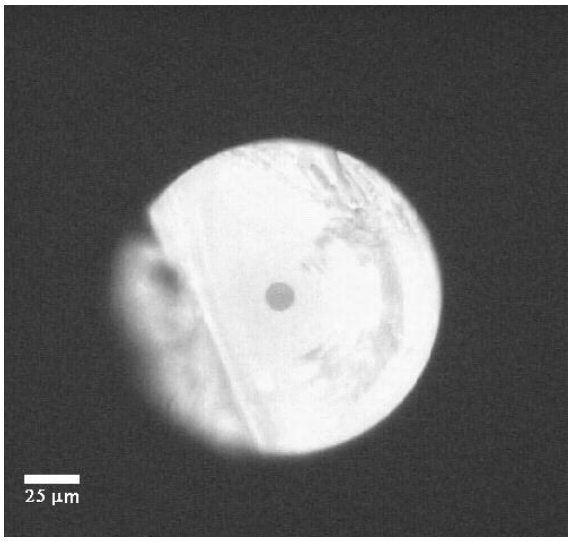

Figure 2: Tellurite glass PbTe doped core/undoped clad optical fiber microphotography with 125 μm outer diameter and 12 μm core diameter.

Thermal analysis: The optical and thermo physical analysis performed indicated that the pair PbO/BaO would be ideal for the core, with compositions 35 TeO_2 - 5 ZnO - 10 CdO - 10 B_2O_3 - (5-35) BaO – (35-5) PbO while the pair B_2O_3/CdO with compositions 35 TeO_2 - 5 ZnO - (0-20) CdO - (20-0) B_2O_3 - 20 BaO - 20 PbO would be ideal for the clad. The Tg and Tx temperatures were obtained by Differential Thermal Analysis (DTA) and the thermal expansion coefficient by Thermo mechanical Analysis (TMA) for all glass compositions. Figures 3 and 4 show the T_g and T_x while Figures 5 and 6 show the expansion coefficient obtained for the core/clad pair. The shadow indicates the composition chosen to the core/clad glasses.

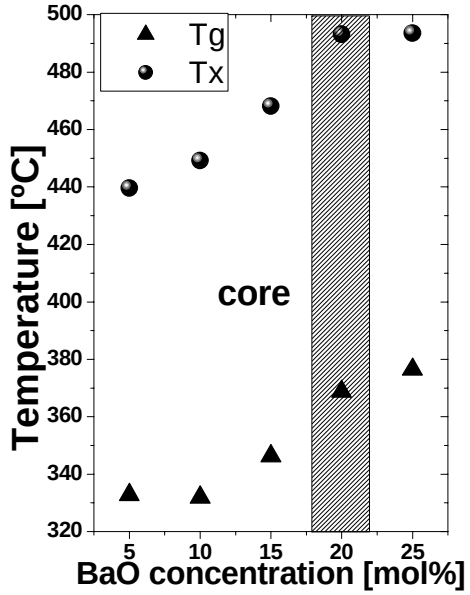

Figure 3: Tg and Tx for the PbTe QD doped core.

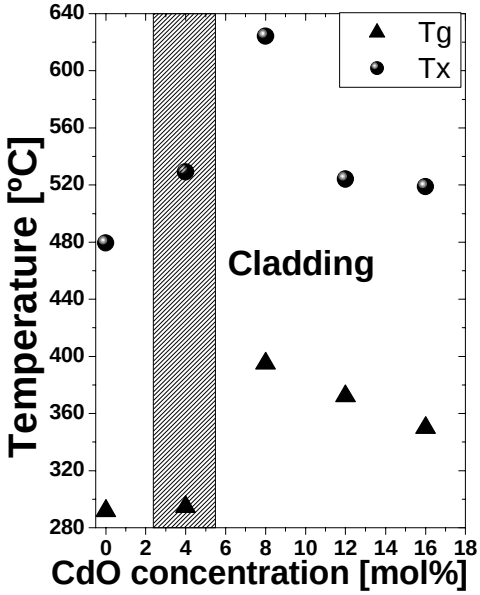

Figure 4: Tg and Tx for the undoped clad

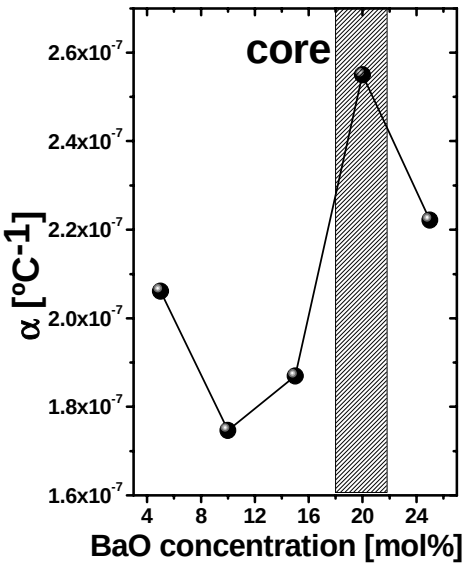

Figure 5: Thermal expansion coefficient for the PbTe QD doped core.

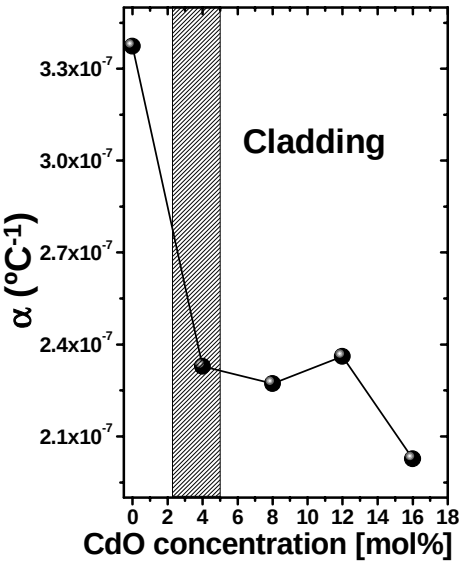

Figure 6: Thermal expansion coefficient for the undoped clad.

The TSR for the clad was 232 K and 132 K for the core, larger than 100 K. Figures 5 and 6 also shows the thermal expansion coefficient matching around $\alpha = 2{,}5.10^{-7}\ ^0C^{-1}$. The final meaning of these four figures show that tellurite PbTe doped core/undoped clad optical fiber is no longer limited by the glasses thermo physical properties.

Optical analysis: besides the thermo physical properties optical fiber requires the control of the refractive indexes. The requirements, in this case, are a little bit less stringent because its is possible to obtain single mode optical fibers by changing the core/clad index variation or the core diameter. The refractive indexes of all 25 compositions were measured with a with a prism coupler METRICOM model 2010 at 632.8 nm, 1305 nm and 1536 nm. The QD doped core measurement was made with heat treated slices of the 8 mm rod and we observed that the QD growth actually decreases the glass refractive index. This is probably due to glass host Pb and Cd extraction to form the QDs, because the refractive index increases with both PbO and CdO contents. Figures 7 and 8 show the results obtained for the doped core at several annealing times and for the clad with different CdO contents. The core refractive index at 1536 nm is 1.825, larger than the 1.80 clad index at the composition indicated by the shadow assuring that the optical fiber can be made from the refractive index point of view also.

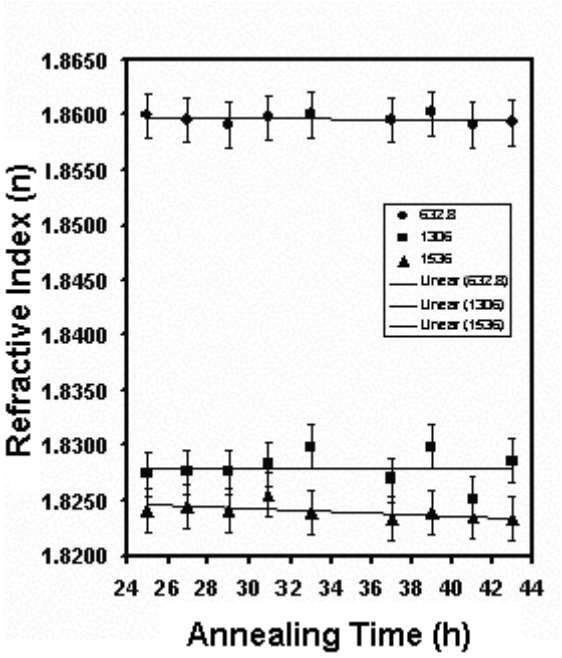

Figure 7: Refractive index for doped preform with quantum dots of PbTe for different thermal treatments (growth of the QD)

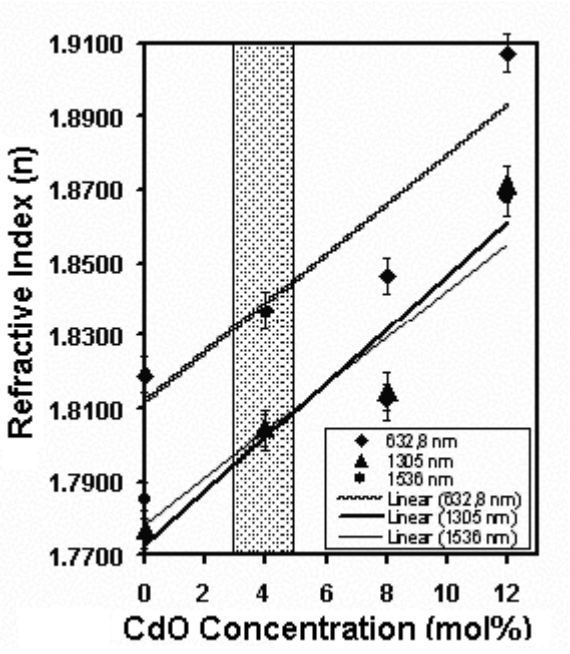

Figure 8: Refractive index of the gladding (pipe) for different CdO concentration.

Quantum Dots characterizations: Only questions respect to the quantum dots quality remains at this point. The quality of the QDs doped bulk glasses annealed at different times was as good as the other PbTe doped glasses we made, as observed by the optical absorption spectra and High Resolution Transmission Electron Microscopy (HRTEM). The slices taken from the rod with posterior QD dot growth at controlled heat treatment also showed good quality QDs. However, the absence of the quenching necessary to vacuum sucking of the rod, the double drawing process and the direct annealing of the core/clad fiber could spoil the QD quality by uncontrolled nucleation/growth or heterogeneous growth at core/clad interface. Therefore, we decided to characterize the optical absorption and the transmission electron microscopy directly of the optical fiber produced.

HRTEM: the sample preparation for HRTEM starts by triturating the optical fiber in dust with smaller than 10 μm grains followed by grinding and dimpling and ion milling and then crunched and diluted in 2-propanol. This solution was dripped into a NaCl crystal and, after NaCl dissolution in water and catched in a cooper net as a free

standing quantum dot glass/carbon film. 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. Figure 9 shows the QD HRTEM microphotography with clear PbTe QDs.

Optical absorption spectroscopy: The quenched and non quenched glasses were compared by the absorption spectra obtained of 1 mm thick glass slides and rod slices extracted from the non quenched rod and treated at the same temperature for the same 25, 27, 29, 31, 33, 35, 38 and 42 hours at a Nicolet (model) Fourier Transform Spectrometer. The non quenched sample presented broader spectra but still with well defined absorption peaks, very different from just the shoulder common to the broad size dispersion QD samples. For the optical fiber direct attenuation spectra we used the following procedure: use a pair of lenses to focus down the FT light beam at the two ends of a 4 mm piece of the optical fiber; collected the background FT spectra with the non annealed optical fiber and, finally, making sure that the FT spectrometer remain unused for the next 31 hours necessary to anneal the optical fiber for the QD growth, obtained the spectrum normalized to the same fiber not annealed. The result is shown by Figure 10 where a clear attenuation peak at 1300 nm can be seen.

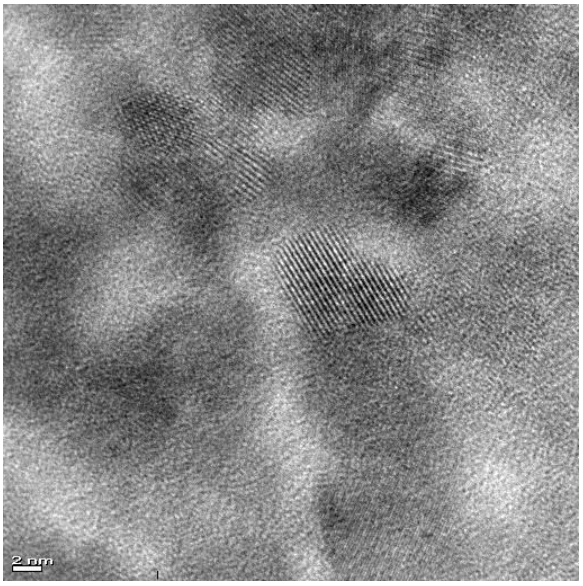

Figure 9: HRTEM of PbTe QD doped tellurite glass optical fiber annealed for 31 hours.

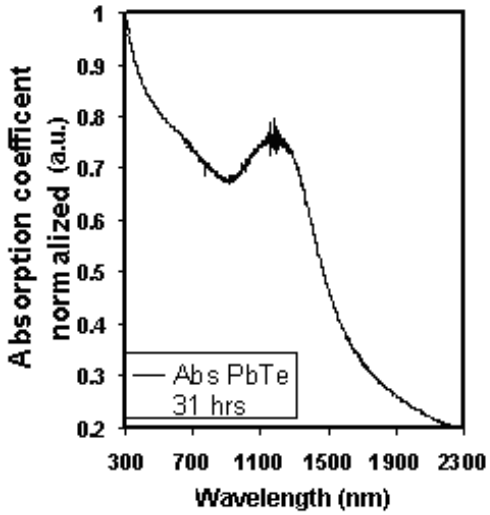

Figure 10: Attenuation spectrum of the 31 hour annealed PbTe QD doped optical fiber.

3 – CONCLUSIONS

We show that it is possible, from any point of view, optical, thermo physical and quantum dot growth quality, to produce 125 μm outer diameter/12 μm core diameter PbTe QD doped core/undoped clad tellurite glass optical fiber. The fact that the produced optical fiber dimensions match the commercial optical fibers means that fiber-fiber optical coupling shall not be an important issue. This optical fiber open up the potential to develop real ultrafast highly non linear all optical devices for optical communications.

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