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Elaboration of multimaterials optical fibers combining tellurite glass and metal for electro-optical applications

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ABSTRACT

The development and the emergence of fully integrated all-fiber optical systems is very interesting from a technical point of view in photonics. Indeed, the development of multimaterials fibers combining both optical waveguide properties and simultaneous in-fiber electrical excitation could provide plenty of innovative signal-processing, sensing or imaging functionalities. Here, we report the engineering of a new glass/metal composite fiber. For the glass, we have chosen tellurite glasses for their excellent thermo-viscous abilities (low T_g) and linear/nonlinear optical properties. This low T_g allows to have a larger panel of potential metals to be co-drawn with. The synthesis is firstly realized by build-in-casting at room atmosphere which allows to get a large-core. Then, the rod-in-tube technique and the insertion of metallic wires allow to get a step-index fiber with a small-core ($7\mu\text{m}$) and two continuous metallic electrodes running along the fiber axis ($\text{Øelectrodes} = 30\mu\text{m}$). Thus, we obtain a tellurite-based core-clad dual-electrode composite fiber made by direct, homothetic preform-to-fiber thermal co-drawing. The rheological and optical properties of the selected glasses allow both to regulate the metallic melting flow and to manage the refractive index core/clad waveguide profile. We will discuss the engineering of these multimaterials optical fibers and their characterization: thermal and viscosity properties, linear optical properties (loss), electrical properties with a continuity of the electrodes over meters of fiber.

Keywords: Hybrid multimaterials optical fibers, electro-optical functionalities, tellurite glasses

1. INTRODUCTION

Multimaterial systems are of great interest in research and industry due to the range of possible perspectives and applications in fields such as medicine, environment or aeronautics. Indeed, the combination of different materials with various properties allows the development of more efficient and compact multifunctional components. Among these systems, the multimaterial fibers are very interesting for the possibility to obtain complex geometry at microscale but also long lengths and a better compacity. These fibers are obtained by the drawing of a macroscopic preform while maintaining the initial geometry. With the significant progress made in fiber drawing processes due to the development of optical fibers for telecommunications, the photonics sector is particularly interested in multimaterial glass/metal fibers in order to combine the remarkable properties of glasses (transparency and light guidance) with those of metal (electrical conduction) to combine an electrical pulse transport function with an optical signal. The idea is to generate electro-optical effects to polarize the medium and create an index variation that would allow the possibility to change the amplitude, phase or path of an optical wave. In the case of a mono-material fiber, the drawing parameters are determined by the viscosity of the material at the drawing temperature. This manufacturing process is ideally suited to amorphous materials such as polymers or glasses which have a wide range of viscosity and softening temperature. Crystalline materials such as metals or semiconductors cannot be drawn separately because of the sudden drop in viscosity above their melting temperature characteristic of a phase transition. In a multimaterial approach, by confining and controlling the crystalline

materials flow in an amorphous support compatible with the drawing, it is possible to design fibers with metal if this one has a melting temperature lower than the drawing temperature [1, 2, 3].

Several glass/metal fibers have already been reported in the literature. These vary according to their geometry, manufacturing techniques and selected materials. Many techniques have been used to insert metal electrodes into a fiber. The most commonly reported method is the pre-drawing of the vitreous support by holding the drilled holes under pressure and then, post-drawing, the liquid metal injection [4, 5]. However, co-drawing of the two materials with the insertion of the metal before drawing allows longer lengths of fibers with electrodes to be obtained [6, 7]. In addition, the main glasses used are silicates whose optical transparency is limited to the visible and near infrared, with weak nonlinear optical properties and strong diffusion of the metal within it altering the optical properties.

Therefore, in this work, we report the development of TeO₂-based glass/metal fibers with much stronger nonlinear optical properties, optical transparency further in the mid infrared and less metal scattering in order to combine an electrical pulse transport function with a broadband optical signal in the mid infrared.

We describe the manufacturing process optimization of these TeO₂-based glass/metal fibers with the enhancement of glass/metal interface quality and mechanical behavior of these fibers by changing the TeO₂-based composition (TeO₂-ZnO-Na₂O [TZN] in TeO₂-ZnO-La₂O₃ [TZL]) with a higher glass transition temperature and better mechanical properties. Previous fibers [4] with TZN exhibited bubbles at the glass/metal interface and the appearance of defects along the electrodes as a result of irregular metal flow during drawing. In addition, the fibers were brittle making them difficult to use. Our new TZL fibers overcome these drawbacks.

2. EXPERIMENTAL SECTION

2.1 Bulk glasses preparation

TZL glasses were prepared at free atmosphere by the conventional melt-quenching technique from mixed precursors. Batches of 10g weight using commercial raw materials TeO₂ (Fox Chemicals, 99%), ZnO (Alfa Aesar, 99,99%), La₂O₃ (Alfa Aesar, 99,99%) and Na₂CO₃ (Alfa Aesar, 99,5%) were loaded in a platinum crucible, then melted at 850°C for 1h in an electric furnace, poured into a brass mold at T_g-30°C and finally annealed at T_g-10°C for 4h to remove any residual internal stress induced by the rapid quench of the glass melt (Figure 1). For the two TZN compositions (80TeO₂-10ZnO-10Na₂O and 70TeO₂-25ZnO-05Na₂O in %mol), there is an additional decarbonation step at 650°C for 30min to remove any residual CO₂ gas from Na₂CO₃ precursor. After synthesis, the obtained glass plates of 15 x 10 x 5 mm³ dimensions were finally polished for the investigations.



Figure 1 : Picture of TZL bulk

2.2 Core-cladding preform preparation and hybrid glass-metal optical fiber drawing

To produce the step-index tellurite glass fibers, the method consists in the combination of two successive steps: Built-in-Casting (BiC) and Rod-in-Tube (RiT) techniques. Firstly, a large-core step-index preform from two different glasses (core and clad) is prepared by BiC as described in Figure 2 [8]. Then, the drawing of this preform allows to obtain 800- μ m thin rods. Finally, a clad preform is mechanically drilled and by RiT the thin clad/core rod is inserted in order to get a small core fiber. During this insertion step, we drilled two more holes on each side of the core to insert two Au₈₀Sn₂₀ alloy wires. We have chosen this alloy for its excellent electrical conduction and its T_m below the drawing temperature allowing the co-drawing.

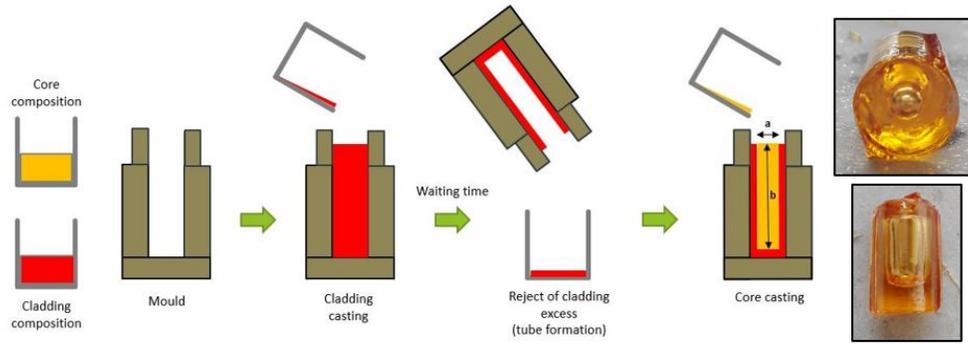


Figure 2 : Core-cladding preform preparation by Built-in-Casting technique

The preform drawing is allowed by using a dedicated 3-meters high optical fiber drawing tower. The preform was slowly fed into the furnace and the temperature was gradually increased up to $\sim 400^{\circ}\text{C}$. The glass was brought to its softening temperature regime while the drawing parameters were continuously monitored to produce the targeted fiber diameter.

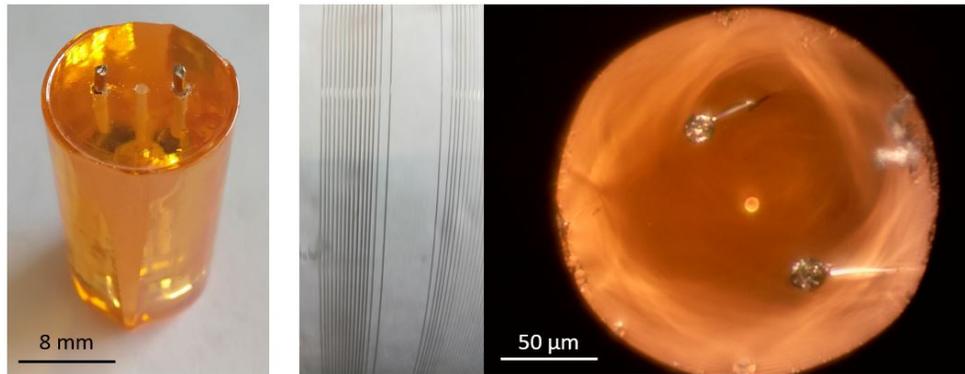


Figure 3 : Hybrid glass-metal preform made by Rod-in-Tube before drawing and view of fiber cross-section

3. RESULTS AND DISCUSSIONS

3.1 $\text{TeO}_2\text{-ZnO-La}_2\text{O}_3$ ternary system investigation

For the optimization of tellurite glass/metal fibers, we decided to change the vitreous matrix by looking for a new TeO_2 -based composition with a higher T_g and higher mechanical properties to facilitate its handling. For this, we turned to TZL compositions which combine these two factors according to Rhonehouse's works [9, 10]. In order to find suitable core and clad compositions for the conception of our multimaterial fibers, we explored the TZL ternary diagram [11] to identify which compositions were vitrified and what the boundaries were (Figure 4). After that, thermal analysis was performed by differential thermal analysis (DSC 2920 TA Instruments) on 20mg samples. Glass transition temperatures were measured as the inflection point of the endotherm at a heating rate of $10^{\circ}\text{C}/\text{min}$ and gathered into a ternary diagram (Figure 4) to show the diversity of T_g that can be obtained with this TZL system creating an impressive range of possibilities and allowing their use in different applications. To select the appropriate compositions, other measurements were performed on each bulk composition (thermal expansion coefficient by dilatometry, transmission by UV-visible and FTIR spectrophotometer, loss by cut-back technique, refractive index at 1550nm using a homemade prism (TiO_2) coupler refractometer, density, Raman analysis and Vickers hardness with a microdurometer). These investigations are detailed and described more extensively in [11].

Another study was carried out in parallel consisting of incorporating Na_2O in small quantities into the selected compositions in order to add Na^+ ions which are migratory species [11]. This aspect can be very interesting for the future

works with the possibility of making thermal poling and second harmonic generation on these multimaterial glass/metal fibers.

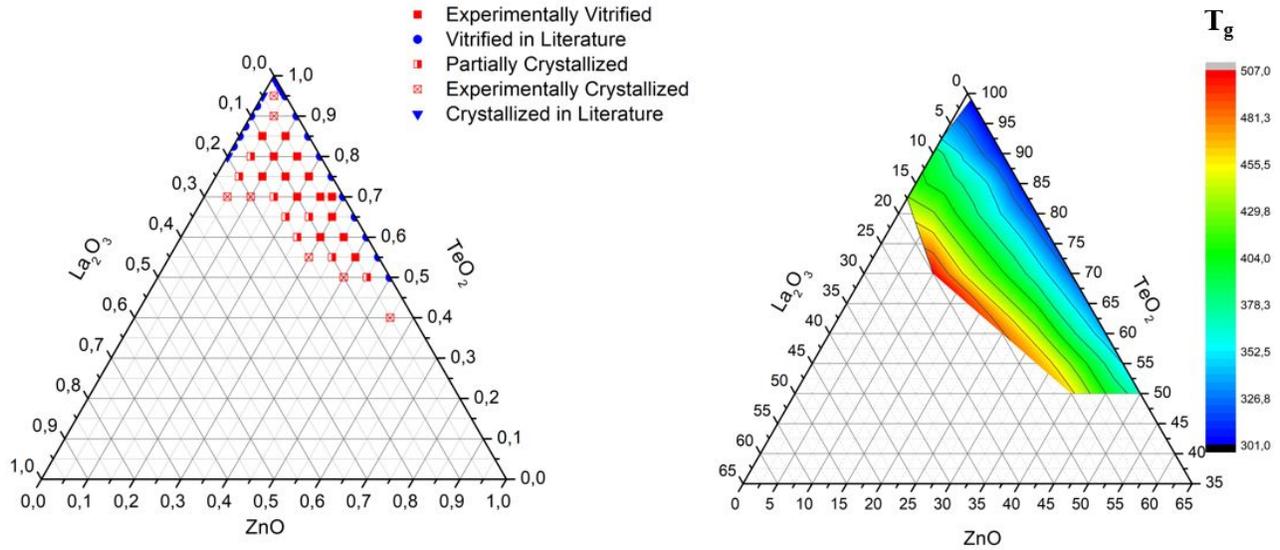


Figure 4 : TZL ternary diagrams: composition influence on the structure and the glass transition temperature

3.2 Cladding and core selections for step-index optical fibers manufacturing

Among the studied compositions of the TZL system, we have selected one core composition and two cladding compositions:

- Core composition: TZL 70-25-05 (%mol)
- Cladding composition: TZL 65-30-05
- Cladding composition: TZLN 68.6-24.5-4.9-2 with small amount of Na₂O for the above reasons

These three compositions were chosen in order to test different fiber geometries (classic step-index and step-index with a W-profile). Their thermal and optical properties are gathered in Table 1. Thermally, these compositions have the advantage of having close fiber drawing temperatures, close thermal expansion coefficients avoiding any fracture and ensuring good cohesion of the assembly and finally a thermal stability (ΔT) higher than 100°C limiting possible surface crystallization. From an optical point of view, refractive index is adapted to ensure the confinement of the light in the core of the fiber, the bulk transmission reaches 6.4 μ m (Figure 5) and minimum losses of 0.8dB/m are obtained at 1.4 μ m.

Table 1 : Thermal and optical properties of TZL and TZLN selected compositions

Composition (mol%)	T _g (°C)	T _x (°C)	$\Delta T = T_x - T_g$ (°C)	Thermal expansion coeff. (°C ⁻¹) (150°C-330°C)	Drawing Temperature (°C) for a 10 ^{5.5} -10 ^{6.5} Poises viscosity	n (1.55 μ m)
TZL 70-25-05	365	525	160	1.143 x 10 ⁻⁵	420-430	1.999
TZL 65-30-05	374	546	172	1.025 x 10 ⁻⁵	425-435	1.980
TZLN 68.6-24.5-4.9-2	357	-	>100	1.084 x 10 ⁻⁵	415-425	1.982

(TZL 70-25-05 = core composition whereas TZL 65-30-05 and TZLN 68.6-24.5-4.9-2 = cladding composition)

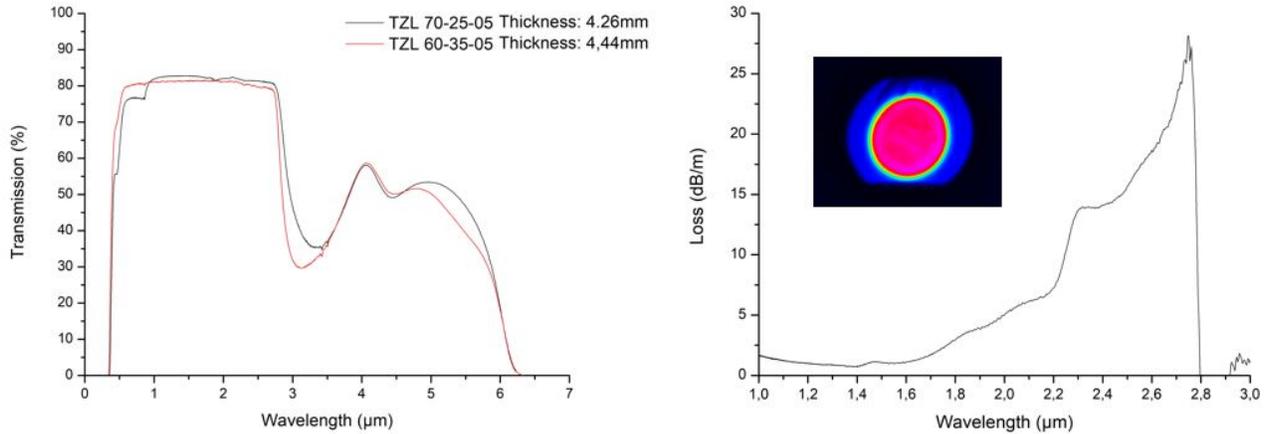


Figure 5 : TZL transmission curve and loss for a step-index fiber with TZL 70-25-05 as core and TZL 65-30-05 as cladding. Picture showing the output beam intensity distribution using a microscope objective and a CCD camera

In addition to thermal and optical measurements, impedance spectroscopy investigations were carried out in order to evaluate the ionic conductivity of the selected compositions and to determine their activation energy (E_a). These two parameters will help us to better understand possible phenomena during future thermal poling and second harmonic generation works. These measurements will be unveiled in a forthcoming publication.

3.3 Hybrid glass/metal fiber characterization

The switch to TZL compositions allows to carry out an annealing before drawing at higher temperature. This annealing improves the adhesion between glass and metal and thus the quality of the interface between the two materials. This change in the manufacturing process results in a more regular metal flow during the drawing process. This reduces defects at the glass/metal interface and irregularities in electrodes diameter. The fibers were observed with a Scanning Electron Microscope (SEM) to check the quality of the interface between the two materials (Figure 6 to the left). These pictures show a suitable quality without defects unlike the TZN-based fibers which presented bubbles (Figure 6 to the right). An additional Energy Dispersive Spectroscopy (EDS) analysis was also performed along the section of the fiber (red line) to detect stoichiometric deviation or inter-diffusion between the glass and electrodes.

Then, to complete the information collected at the SEM on the quality of the glass/metal interface, Atomic Force Microscopy (AFM) was employed to observe the topography of the surface and the phase with a Veeco and phase contrast microscope (Figure 7). The AFM confirms the improvement in the quality of the glass/metal interface. Nevertheless, slight metallic deposits from the electrode can be seen on the glass. Subsequently, it will be necessary to evaluate the diffusion of the metal in the glass to quantify how it alters the optical properties of the fiber.

In order to verify the continuity of the electrode, electrical measurements were performed by applying silver lacquer or an InGa mixture to the ends of several fiber lengths. Thus, the continuity of the $Au_{80}Sn_{20}$ electrodes along the fiber could be checked with a multimeter by detecting a resistance. Initially, we were able to demonstrate that we obtain several tens of meters of fibers with embedded electrodes. Then, by measuring the resistance of several fiber lengths with various electrode diameters, an average resistivity of $2.53 \times 10^{-7} \Omega \cdot m$ was determined. This value is very closed to that given by the supplier of $Au_{80}Sn_{20}$ raw wire ($1.68 \times 10^{-7} \Omega \cdot m$). C. Strutynski [7] had noticed a discrepancy in these resistance values and proposed an explanation with a possible contamination of the metallic electrode or a generation of grain boundaries within the metal during drawing. By optimizing the glass/metal interface, we have overcome this discrepancy.

Finally, these fibers are mechanically more robust and easier to handle. Mechanical tests (tensile strengths and critical bending radius) on these fibers are underway to show the mechanical reinforcement with the transition to TZL compositions. These tests will also be unveiled in an upcoming publication [11].

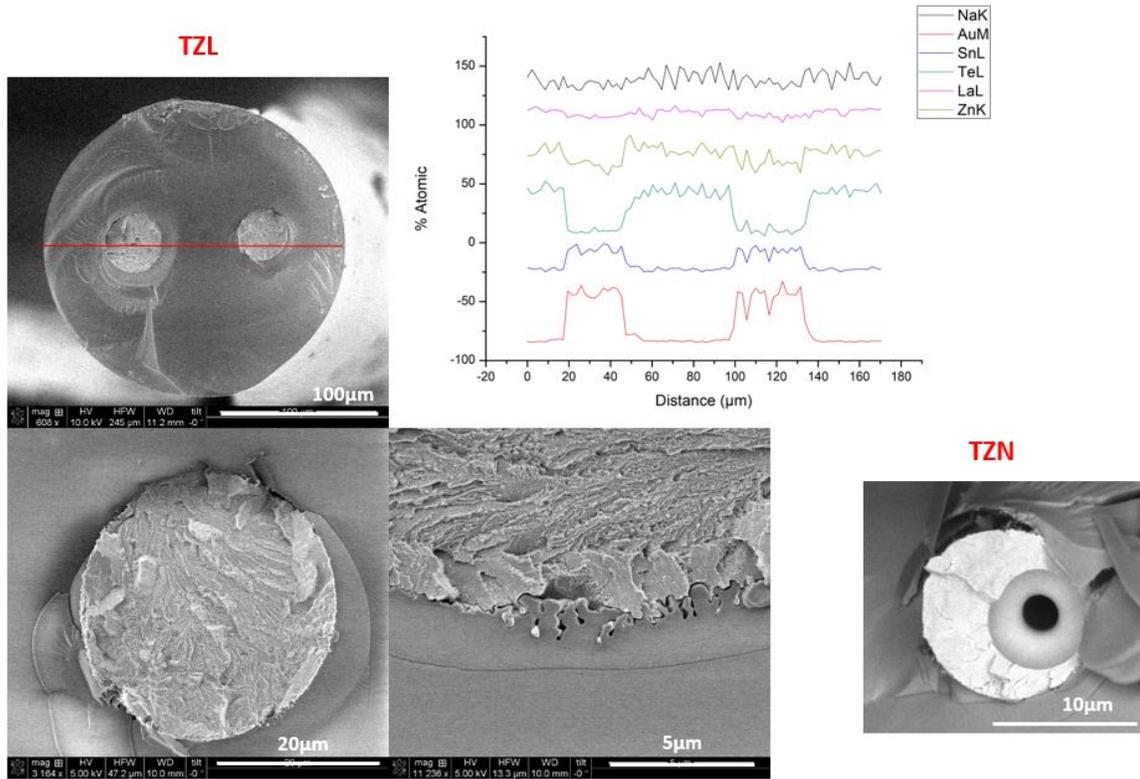


Figure 6 : SEM pictures of hybrid glass/metal optical fibers (TZL to the left and TZN to the right) and EDS measurement on the cross section (red line)

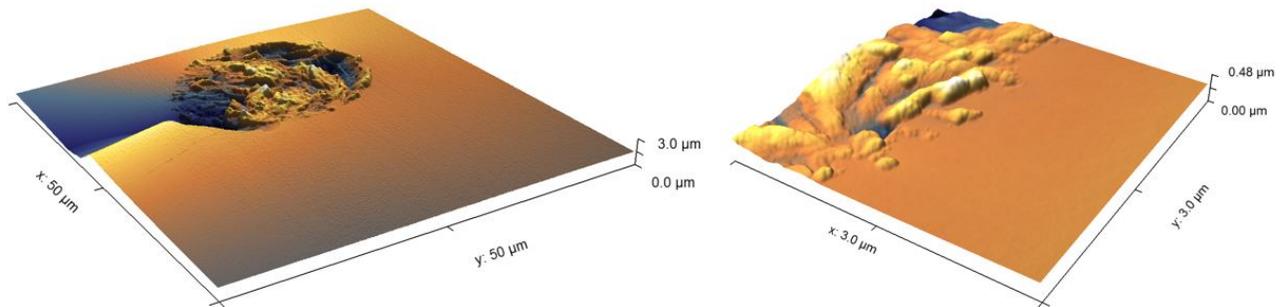


Figure 7 : AFM measurements: topography of the surface (above and to the left) and phases (to the right)

Computer-assisted finite element simulations with the LISA software were also performed by applying a voltage of 100V to the two electrodes (Figure 8). The objective was to understand how the electric potential and the electric field behaved over the fiber cross-section and to evaluate the order of magnitude of the electric field at the optical core. Indeed, the electrodes must be close enough to maximize the electric field between them but far enough from the core to avoid inducing additional optical losses. It is therefore important to find a compromise between the electrode-to-electrode distance, the electrode-to-core distance and the glass breakdown voltage.

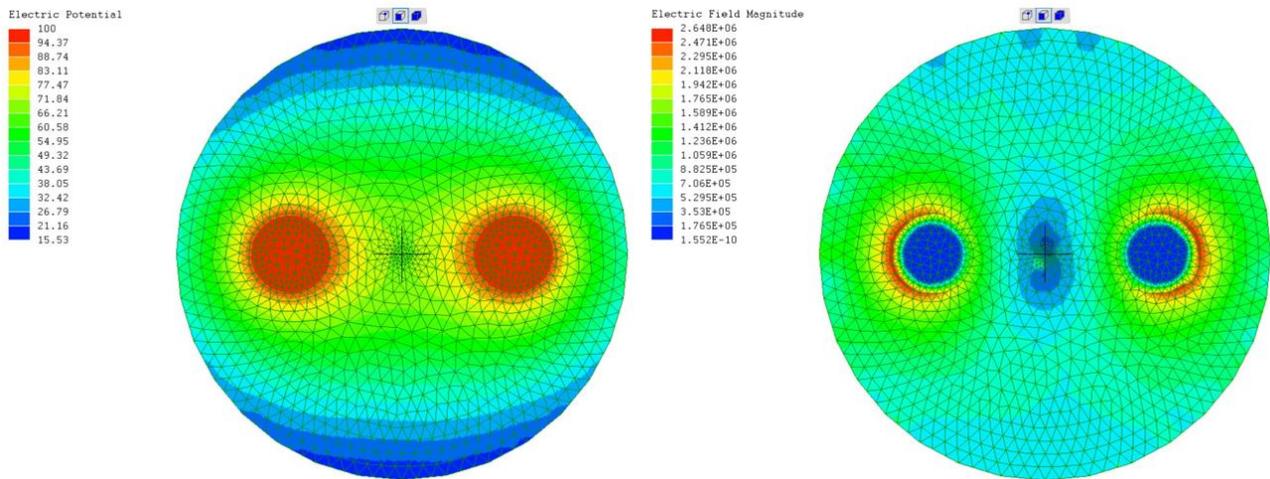


Figure 8 : Application of a 100V-voltage to the two electrodes by computer simulation with the LISA software to see the electric potential and electric field magnitude behavior on the fiber cross-section

3.4 Electrode connectivity to a closed circuit to study Static Kerr effect

The connection of the electrodes to a closed circuit is a crucial and essential parameter for the use of these hybrid fibers. The first method is to connect the electrodes to the fiber ends through a micro-station equipped with tungsten tips connected to a DC voltage generator. The tips are affixed to the fiber electrodes using a microscope.

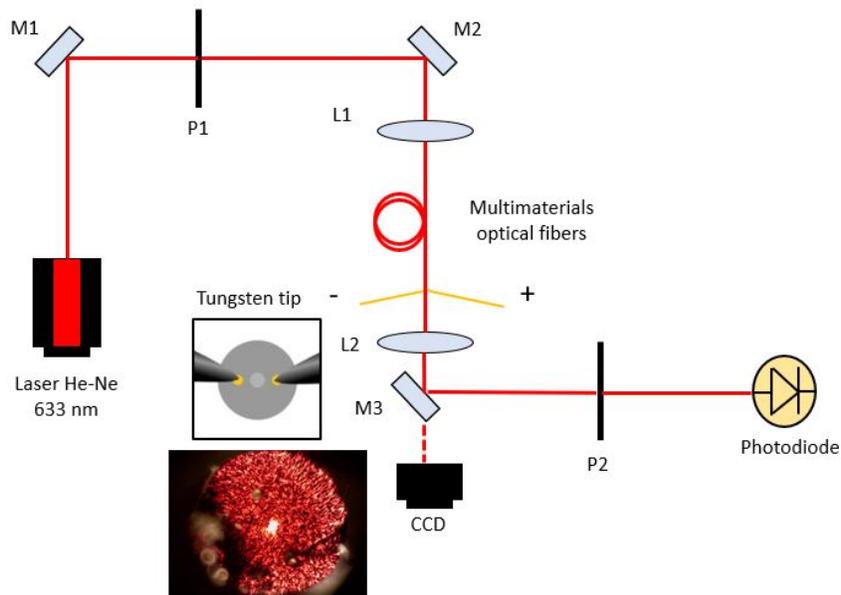


Figure 9 : Setup for measuring the static Kerr effect by connecting the electrodes with a tungsten-tipped micro-station at the fiber end. (Mirror: M1, M2 and M3; Polarizer: P1 and P2; Lens: L1 and L2)

The drawback of this technique is the possible contact loss of the first electrode when connecting the second one. This technique is used to study the electro-optical Kerr effect and calculate the Kerr constant (setup detailed in Figure 9). Measurements are actually under way.

CONCLUSION AND FUTURE WORKS

We have therefore reported here on the optimization of the manufacturing of tellurite-based dual-electrodes core-clad composite fibers. The engineering of these multimaterial glass/metal fibers is based on the drilling of a cladding preform and the insertion of a core rod and two Au₈₀Sn₂₀ metallic wires. This alloy has been chosen to be thermally compatible with the selected glassy matrix in order to have a co-drawing with the glass which supports the flow of metal during the drawing process. By proceeding in this way, we were able to obtain long lengths of optical fibers with continuous embedded metallic electrodes. The transition from TZN to TZL made it possible to carry out annealing before drawing, thus reducing the appearance of defects and irregularities at the glass/metal interface along the fiber as well as possible contaminations that would disturb the optical and electrical properties of the composite fiber. Furthermore, this transition allows also to improve its mechanical properties and its handling for the future works. The optical properties of the fibers can be further improved by the purification of the glasses used by preparing them in controlled atmosphere (glovebox) with higher purity precursors in order to limit parasitic absorptions from OH species and transition metals.

In the future works, the technique to connect the electrodes to a closed circuit has to be enhanced and developed in order to study different nonlinear optical effects like Kerr static effect and measure the Kerr coefficient of these hybrid fibers by controlling the refractive index variation into the fiber thanks to an external electrical excitation.

Potential applications of these hybrid tellurite glass/metal fibers could be electro-endoscopes for medical treatment or frequency doubling and electro-optical modulators for telecommunications.

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