

# USE OF CsCl TO ENHANCE THE GLASS STABILITY RANGE OF TELLURITE GLASSES FOR Er<sup>3+</sup> DOPED OPTICAL FIBER DRAWING

Carmen Rosa Eyzaguirre<sup>1</sup>, Eugenio Rodriguez<sup>1</sup>, Enver Fernandez Chillece<sup>1</sup>, Sérgio Paulo Amaral Osório<sup>1</sup>, Carlos Lenz Cesar<sup>1</sup>, Italo Odone Mazali<sup>2</sup>, Oswaldo Luiz Alves<sup>2</sup> and Luiz Carlos Barbosa<sup>1,\*</sup>

<sup>1</sup> Departamento de Eletrônica Quântica, Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas - UNICAMP, Campinas, SP, Brazil.

<sup>2</sup> Laboratório de Química do Estado Sólido, Instituto de Química, Universidade Estadual de Campinas - UNICAMP, Campinas, SP, Brazil.

## ABSTRACT

Tellurite glasses are important as a host of Er<sup>3+</sup> ions because of their great solubility and because they present broader gain bandwidths than Er<sup>3+</sup>-doped silica, with promise to increase the bandwidth of communication systems. However, the small glass stability range (GSR) of tellurite glasses compromises the quality of the optical fibers. We show that the addition of CsCl to tellurite glasses can increase their GSR, making it easier to draw good quality optical fibers. CsCl acts as a network modifier in glass systems, weakening the network by forming Te-Cl bonds. We show that the thermal expansion coefficient mismatch is in the right direction for optical fiber fabrication purposes and that the Bi<sub>2</sub>O<sub>3</sub> content can be used to control the refractive index of clad and core glasses. Single-mode and multi-mode Er<sup>3+</sup>-doped optical fibers were produced by the rod-in-tube method using highly homogeneous TeO<sub>2</sub>-ZnO-Li<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub>-CsCl glasses. Far infrared spectra of the glass samples exhibit absorption bands of the Te-Cl bond.

## 1. INTRODUCTION

Tellurite glass optical fibers are important for telecommunications because the Er<sup>3+</sup> ion fluorescence bandwidth at 1550 nm in this host is much broader than in other glasses at the same time that the solubility limit for the rare earth is much higher.<sup>1,2</sup> This means that it can be doped up to 70000 ppm, allowing higher gain per unit length.<sup>3</sup> This fact can be understood considering that Er<sub>2</sub>O<sub>3</sub> is actually a glass former and not only a dopant in this kind of glass. The glass could even be called TeO<sub>2</sub>-Er<sub>2</sub>O<sub>3</sub> glass. Used in optical amplifiers these fibers would show broader band optical amplification for Wavelength Division Multiplexing (WDM) systems, increasing the number of wavelengths of the optical channels from those of the usual Er<sup>3+</sup>-doped silica fibers.<sup>3,4</sup> Moreover, due to the higher doping level, these devices should require centimeter long optical fibers, instead of the usual tens of meter scale length used up to now.<sup>5,6,7</sup>

However, optical fiber production with this glass has been a challenge mainly due to its low glass stability range that leads to crystallization processes at the moment of optical fiber drawing. The two other problems one has to face are how to control the difference in refractive index and the expansion coefficient mismatch between the core and the clad glasses of the optical fibers. Since the possibility of large amplification bandwidth has been recognized, several tellurite glass compositions have been tried, among them the TeO<sub>2</sub>-ZnO-Na<sub>2</sub>O-Er<sub>2</sub>O<sub>3</sub> and TeO<sub>2</sub>-WO<sub>3</sub>-Er<sub>2</sub>O<sub>3</sub> families generated international patents<sup>8,9</sup> and used the Bi<sub>2</sub>O<sub>3</sub> content to control the core/clad refractive index and viscosity. The Corning group also used the Nb<sub>2</sub>O<sub>5</sub> content for this purpose.

The aim of this paper is to show that glass stability range (GSR) of tellurite glasses can be enhanced by adding CsCl, without losing any of the other characteristics of the tellurite glasses that made it promising for Er<sup>3+</sup>-doped optical amplifiers. To show this we present the thermo-physical results obtained with bulk TeO<sub>2</sub>-ZnO-Li<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub>-CsCl (TeZnLiBiCsCl) glass samples and the Er<sup>3+</sup> doped optical fiber produced with them by the rod-in-tube method.

## 2. EXPERIMENTAL PROCEDURE

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\* Corresponding address e-mail: [barbosa@ifi.unicamp.br](mailto:barbosa@ifi.unicamp.br)

To synthesize the TeZnLiBiCsCl glass samples we melted powdered chemical compounds with 99.999% purity in gold crucibles at 1023 K in a resistance furnace in an oxygen-controlled atmosphere over 2 h. After fusion the glass was quenched in stainless steel molds, followed by a thermal treatment (annealing) at 513 K for 2 h to avoid the formation of internal stresses, and then cooled naturally to room temperature. Tables I and II show the nominal compositions of the several samples synthesized. The compositions of TeZnLiBiCsCl glasses were analyzed by X-ray fluorescence (XRF) spectroscopy (EDX 700 Shimadzu). Although it is a semi-quantitative technique, it was found that the composition change due to vaporization was limited (the loss of Cl and Cs were less than 6% for all samples). Similar results were also reported by Ding and coworkers.<sup>10</sup>

Table I. Nominal composition of the TeZnLiBiCsCl glass systems with different concentrations of CsCl, all doped with 10000 ppm of erbium.

Sample code	Nominal Composition (mol%)				
	TeO <sub>2</sub>	ZnO	Li <sub>2</sub> O	Bi <sub>2</sub> O <sub>3</sub>	CsCl
TeZnLiBiCsCl-a	78.0	15.5	5.0	1.5	0.0
TeZnLiBiCsCl-b	72.5	15.5	5.0	1.5	5.5
TeZnLiBiCsCl-c	70.5	15.5	5.0	1.5	7.5
TeZnLiBiCsCl-d	68.5	15.5	5.0	1.5	9.5
TeZnLiBiCsCl-e	65.5	15.5	5.0	1.5	12.5

Table II. Nominal composition of the TeZnLiBiCsCl glass system with different concentrations of Bi<sub>2</sub>O<sub>3</sub>, all doped with 10000 ppm of erbium.

Sample Code	Nominal Composition (mol%)				
	TeO <sub>2</sub>	ZnO	Li <sub>2</sub> O	Bi <sub>2</sub> O <sub>3</sub>	CsCl
TeZnLiBiCsCl-A	70.0	15.5	5.0	0.0	9.5
TeZnLiBiCsCl-B	69.0	15.5	5.0	1.0	9.5
TeZnLiBiCsCl-C	68.5	15.5	5.0	1.5	9.5
TeZnLiBiCsCl-D	68.0	15.5	5.0	2.0	9.5
TeZnLiBiCsCl-E	67.5	15.5	5.0	2.5	9.5

The non-crystallinity of the samples was confirmed by X-ray diffraction analysis using CuK $\alpha$  radiation with a Philips PW1820 diffractometer. Typical temperatures related with glass stability: T<sub>g</sub> (glass transition temperature), T<sub>x</sub> (onset of crystallization temperature) and T<sub>m</sub> (melting temperature) were measured by differential thermal analyses (DTA, Shimadzu Ta-50WS), while T<sub>d</sub> (softening dilatometric point) and  $\alpha$  (thermal expansion coefficient) were measured by thermo mechanical analyses (TMA, Shimadzu TA 50WS). The DTA measurements were done with both powdered (particle diameter around 64  $\mu$ m) and bulk glass samples using a heating rate of 10 K $\cdot$ min<sup>-1</sup> under an argon atmosphere (20 mL $\cdot$ min<sup>-1</sup>). To measure the thermal expansion coefficient by TMA, we used cylindrical samples with polished parallel faces.

The refractive indices (n) were measured using a prism-coupling method at 632.8, 1305.4 and 1536.0 nm on polished glass samples. A Metricon model 2010 Prism Coupler instrument, with index accuracy of 0.0001, was used. The structural characterization of the glass samples was performed using a DA8 BOMEN FTIR spectrometer operating in the 100-600 cm<sup>-1</sup> region and with 4cm<sup>-1</sup> resolution. For that purpose the powdered glass samples were mixed with KBR glass and finally pressed to form 1mm thick pellets.

Single-mode and multiple-mode optical fibers were fabricated by the rod-in-tube method. The rod and the tube were just sucked from the melt into the interior of a silica tubes with different diameters with a dentist's vacuum pump. The tellurite glasses come out from the silica tube during the cooling process due to their very different expansion coefficient. The cladding tube composition was 68.5TeO<sub>2</sub>-15.5ZnO-5Li<sub>2</sub>O-1.5Bi<sub>2</sub>O<sub>3</sub>-9.5CsCl (mol%) and the 0.3 mm rod for the core had a 68TeO<sub>2</sub>-15.5ZnO-5Li<sub>2</sub>O-2Bi<sub>2</sub>O<sub>3</sub>-9.5CsCl (mol%) glass composition doped with 10000 ppm erbium. Both glasses, the rod and the tube, received a 2 h thermal treatment at 513 K.

A 125  $\mu$ m outer diameter and 35  $\mu$ m core diameter multimode optical fiber and a 125  $\mu$ m outer diameter and 12  $\mu$ m core diameter single-mode optical fiber were drawn with this clad-core system using a Heathway fiber-drawing

tower at a  $2.3 \text{ m}\cdot\text{min}^{-1}$  drawing velocity. The  $\text{Bi}_2\text{O}_3$  content was used to control the clad-core refractive index differences and to assure the single-mode operation. The light guided by an optical fiber will be single mode when  $V \leq 2.405$ , where  $V = \frac{2\pi a}{\lambda} NA$  is the optical fiber V-parameter,  $a$  = fiber core radius,  $\lambda$  = vacuum wavelength and  $NA = \sqrt{n_{\text{core}}^2 - n_{\text{clad}}^2} \cong \sqrt{2 n_{\text{clad}} \Delta n}$  is the fiber numerical aperture.<sup>11</sup> The attenuation spectrum of the fiber doped with 10000 ppm of  $\text{Er}^{3+}$  was obtained with an optical spectrum analyzer, HP 71451A Instrument Modes, using a white light source and a commercial silica fiber of  $9 \mu\text{m}$  core diameter and  $125 \mu\text{m}$  total diameter as a reference.

### 3. RESULTS

The results of XRF analysis revealed that the difference between the nominal composition and synthesized  $\text{TeZnLiBiCsCl}$  glasses was within 6%, independent of the CsCl content, indicating that the composition change because of vaporization of CsCl was limited.<sup>12</sup> According to this; the sample composition is expressed by the nominal composition.

The  $\text{TeZnLiBiCsCl}$  glasses are totally free of gross defects (such as bubbles, seeds and *stones* – particles of undissolved in material), *striae*, cords and in homogeneities. For this reason, we classify the  $\text{TeZnLiBiCsCl}$  glasses as highly homogeneous. All the  $\text{TeZnLiBiCsCl}$  glasses showed XRD patterns (not shown here) typical of non-crystalline solids, presenting a broad peak near  $2\theta = 28^\circ$ .

Fig. 1 shows the DTA curves for powdered  $\text{TeZnLiBiCsCl}$  glasses with different CsCl content, as indicated in Table I. The baselines of the DTA curves were corrected to obtain just a horizontal curve until the first exothermic event using the equation  $Q = (a + bT + cT^2) \cdot Q_m$ , where T is the temperature, Q and  $Q_m$  are the signal after and before the correction and a, b and c are obtained with a fitting, as recommended by the Instruction Manual of the Manufacturer. The dashed lines were drawn just to guide the eyes for the enhanced glass stability range (GSR) as the CsCl content increases.

Each DTA curve shows four thermal events. The first one is endothermic and it is related to  $T_g$ . The second one is also an endothermic event and it can be explained as a result of softening and sintering of the powdered glass samples.<sup>13,14</sup> The third and fourth events are related to  $T_c$  and  $T_m$ , respectively.

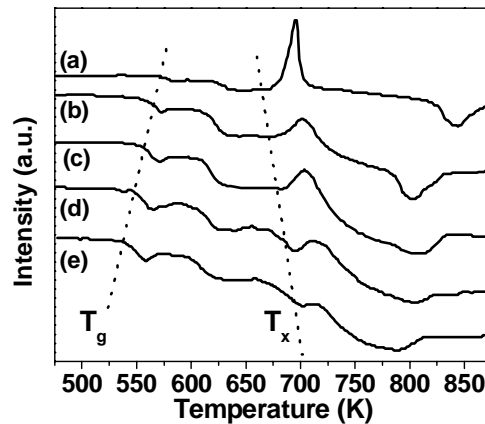


Figure 1: DTA curves of the  $\text{TeZnLiBiCsCl}$  glass systems with different concentrations of CsCl.

In glasses, sintering takes place by the viscous flow of a glass phase and the densification phenomena occurs by coalescence process, which start with the formation of necks between particles.<sup>13</sup> To prove that the second thermal event observed in the DTA curve is related to sintering and not related to a second  $T_g$ , powdered  $\text{TeZnLiBiCsCl}$  glass samples ( $149 \mu\text{m}$  mesh) were compacted and underwent thermal treatments at 621 K for 10 min. The sample surface was analyzed by scanning electron microscopy. The SEM image (Fig. 2) clearly shows neck formation, indicating the softening of the glass and the subsequent coalescence between particles, typical of sintering processes.

From the first, third and fourth thermal events observed in the DTA curves, we determined the  $T_g$ ,  $T_x$ , and  $T_m$ , from which we extracted the glass stability range,  $GSR = T_x - T_g$ , and the Hrubý number,  $H_r = \frac{T_x - T_g}{T_m - T_x}$ ,<sup>15</sup> shown in

Table III. The  $T_d$  and  $\alpha$  are plotted as a function of the CsCl content in Fig. 3. The optical fiber can be produced only when the core thermal expansion coefficient is larger than the clad one, allowing it to collapse inside the clad. Table IV shows the core and clad expansion coefficients and their refractive indices at 1536 nm.

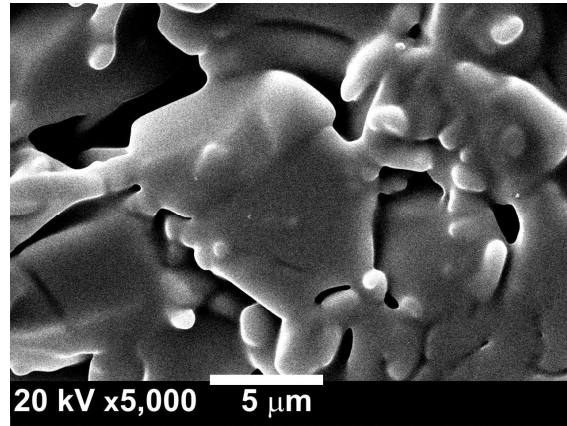


Figure 2: SEM micrograph of a compacted powdered TeZnLiBiCsCl glass [sample Fig. 1(c)] after thermal treatment at 621 K for 10 min.

Table III.  $T_g$ ,  $T_x$ ,  $T_m$ ,  $T_d$ ,  $\alpha$ , GSR and  $H_r$  for TeZnLiBiCsCl glass system with different concentrations of CsCl.

Code Sample*	$T_g \pm 1$ (K)	$T_x \pm 1$ (K)	$T_m \pm 1$ (K)	GSR $\pm 1$ (K)	$H_r$	$T_d \pm 1$ (K)	$\alpha$ ( $10^{-5} K^{-1}$ )
TeZnLiBiCsCl-a	571	676	819	105	0.72±0.01	589	1.55 ± 0.05
TeZnLiBiCsCl-b	557	679	784	122	1.16±0.02	580	1.73 ± 0.05
TeZnLiBiCsCl-c	554	693	790	129	1.43±0.02	578	1.83 ± 0.05
TeZnLiBiCsCl-d	546	692	777	145	1.72±0.03	578	1.98 ± 0.06
TeZnLiBiCsCl-e	536	696	774	160	2.05±0.04	572	2.10 ± 0.06

\* Typical temperatures related with glass stability were extracted from DTA curves of the Fig.1.

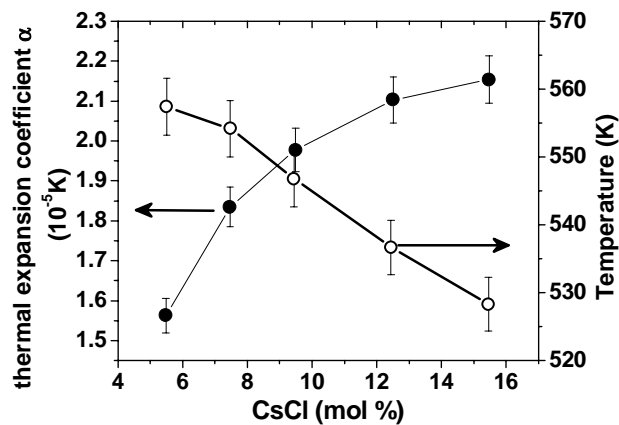


Figure 3: Variation of the  $\alpha$  and  $T_g$  in the TeZnLiBiCsCl glass systems with different concentrations of CsCl.

Table IV.  $\alpha$ ,  $n$  and  $T_g$  of both cladding and core of optical fibers fabricated by the rod-in-tube method.

	$\alpha$ ( $10^{-5} \text{ K}^{-1}$ )	$n \pm 0.0001$ ( $\lambda = 1536 \text{ nm}$ )	$T_g \pm 1$ (K)
Cladding	$2.09 \pm 0.06$	1.9407	546
Core	$2.32 \pm 0.07$	1.9430	545

Table V shows the values for the core refractive index,  $n$ , as a function of the  $\text{Bi}_2\text{O}_3$  content for the 632.8, 1305.4 and 1536 nm wavelengths. The optical fiber numerical aperture  $\text{NA} = 0.09$ , extracted from these data is used to calculate a core radius of  $a = 12 \mu\text{m}$  to produce a single-mode optical fiber with the  $V$ -parameter  $V = 2.2$  at 1536 nm.

Table V. Refractive indices ( $n$ ) of TeZnLiBiCsCl glass system with different concentrations of  $\text{Bi}_2\text{O}_3$ .

Sample Code	Refractive Index, $n \pm 0.0001$		
	632.8 nm	1305.4 nm	1536 nm
TeZnLiBiCsCl-A	1.9812	1.9372	1.9328
TeZnLiBiCsCl-B	1.9873	1.9427	1.9381
TeZnLiBiCsCl-C	1.9899	1.9452	1.9408
TeZnLiBiCsCl-D	1.9926	1.9477	1.9430
TeZnLiBiCsCl-E	1.9956	1.9502	1.9456

For the multi-mode fiber this parameter is  $V = 6.4$ , also at 1536 nm. Fig. 4 shows the attenuation spectrum of the single-mode optical fiber, showing the characteristic bands of the  $\text{Er}^{3+}$  ion in the 980 nm and 1540 nm regions.

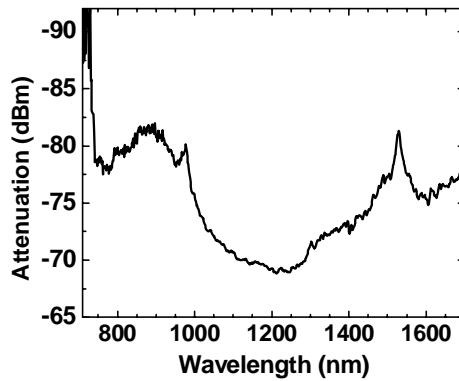


Figure 4: Attenuation curve as a function of the wavelength for the single-mode optical fiber.

#### 4. DISCUSSIONS

The DTA curves of Fig. 1 show a displacement of  $T_g$  to lower temperatures and  $T_x$  to higher temperatures as the content of CsCl is increased up to 12.5 mol%, opening up the GSR of this glass from 378 K to 433 K. Our interpretation of the GSR increasing with the CsCl content is as follows. The CsCl opens up the glass network by changing the trigonal bipyramid  $TeO_4$  to the trigonal pyramid  $TeO_3$ , decreasing  $T_g$ . The Cl electro negativity is strong enough to replace the oxygen bond in  $TeO_2$  by TeCl while the heavy Cs element keeps the other atoms apart, avoiding crystallization and increasing  $T_x$ . The heavy element does not allow the glass network to close in small units, keeping its vitreous character. This interpretation is further justified by the TMA results (Table III). The  $T_d$  decrease with increasing CsCl content was expected because  $T_d$  and  $T_g$  are closely related. On the other hand,  $\alpha$  increases with the CsCl concentration, indicating a weakening of the bonds such as the one produced by the substitution of Te-O by the weaker Te-Cl bonds. To demonstrate the presence of Te-Cl bonds, FTIR measurements were performed at two glass samples doped with 10 000 ppm of  $Er^{3+}$  one of them without CsCl compound. Results of these measurements are presented in figure 5. The arrows in the sample containing CsCl around  $112\text{ cm}^{-1}$  and  $158\text{ cm}^{-1}$ , respectively could indicate the presence of the Te-Cl bond. It is possible to estimate theoretically if those two peaks really belong to the Te-Cl bonds.<sup>16,17,18</sup> For that purpose we used

the relation of the vibrations frequency ( $\nu$ ) as function of the bonding force ( $K$ ) and the affective mass( $\mu$ ),  $\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$ .

Furthermore it was assumed the bonding force as been  $K = 5.288 \times N \times \left( \frac{\chi_{Cl} \chi_{Te}}{d^2} \right)^{\frac{3}{4}} + 30\text{ Nm}^{-1}$ , where  $N = 1$  for

covalent bonds,  $d$  is the bonding distance between Te-Cl and  $\chi_{Cl}$ , and  $\chi_{Te}$  are the Cl e Te ions electro negativities, respectively.

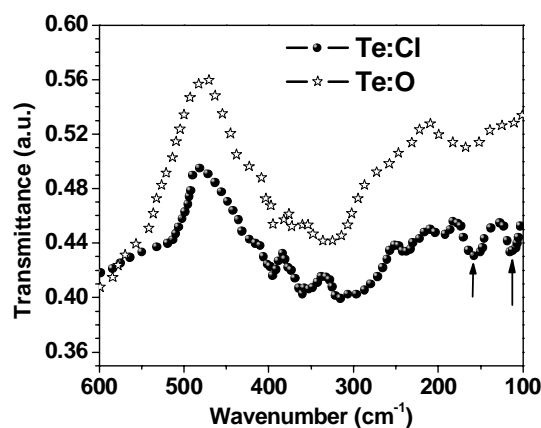


Figure 5: FTIR spectra of the TeO<sub>2</sub>-ZnO-Na<sub>2</sub>O-CsCl and TeO<sub>2</sub>-ZnO-Na<sub>2</sub>O glass samples doped with 10000 ppm Er<sup>3+</sup>

Calculations yielded results around 130cm<sup>-1</sup> for the Cl-Te vibration frequency which well agree with the values observed in the FTIR spectra of the glass samples shown in figure 5. It is noteworthy to remember that the cesium molecular mass is greater than the oxygen one. In this sense the Cl ions acts as a modifier of the network similar to heavy metal oxide glasses where the network modifier acts as a network depolymerizer.<sup>19,20</sup> The presence of the Te-Cl was many time ago observed by Adams<sup>21</sup> et al in solutions of hexachlorotellurates.

The H<sub>r</sub> number for all glass compositions, shown in Table III, is greater than 0.1 and some are larger than one. Accordingly to Hrubý, glasses with H<sub>r</sub> less than 0.1 are difficult to prepare and require rigorous control of the experimental conditions, glasses with H<sub>r</sub> = 0.5 are easily prepared.<sup>15</sup> Although Hrubý attributed H<sub>r</sub> numbers larger than one to high-molecular polymer-type glasses,<sup>15</sup> our results show a depolymerization of the vitreous network.

The lack of bubbles, crystallized particles and striations show a good glass for optical fiber guiding purposes. The clad-core refraction index step can be controlled by the Bi<sub>2</sub>O<sub>3</sub> content which follows a linear behavior for contents below 3 mol% and reaches saturation above 4 mol%. Thus we can control the refractive index difference by keeping the Bi<sub>2</sub>O<sub>3</sub> content of the core and clad at 0.5 mol%. The optical fiber NA can be obtained from n versus the Bi<sub>2</sub>O<sub>3</sub> content curve and it be used to calculate the core diameter to produce a single-mode optical fiber. For the NA = 0.09 and a 12 mm core diameter we obtain V = 2.2 for the single-mode fiber V-parameter, which means that 78% of the light power would transmit through the core and 22% through the clad.<sup>22</sup>

## 5. CONCLUSIONS

We have shown that the promise of tellurite glasses for very large bandwidth optical amplifiers can be fulfilled by increasing its glass stability range to produce better optical fibers. We also show that the addition of CsCl to the original composition can enhance the GSR. We produced single-mode and multi-mode optical fibers using highly homogeneous (78-x)TeO<sub>2</sub>-15.5ZnO-5Li<sub>2</sub>O-1.5Bi<sub>2</sub>O<sub>3</sub>-xCsCl (mol%) and (70-x)5TeO<sub>2</sub>-15.5ZnO-5Li<sub>2</sub>O-xBi<sub>2</sub>O<sub>3</sub>-9.5CsCl (mol%) glasses and investigated the role of the CsCl their GSR. We observed that CsCl acts as a network modifier in glass systems, weakening the network by forming Te-Cl bonds. Furthermore, the presence of Te-Cl bonds was demonstrated by studying the far infra-red spectra of the glass samples. We show that the thermal expansion coefficient mismatch is in the right direction for optical fiber fabrication purposes, that is, the core coefficient is larger than the clad one. We also show that the Bi<sub>2</sub>O<sub>3</sub> content can be used to control the refractive index of clad and core glasses and have produced both, single-mode and multi-mode optical fibers with Er<sup>3+</sup>-doped tellurite glasses.

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