

Use of CsCl to Enhance the Glass Stability Range of Tellurite Glasses for Er³⁺-Doped Optical Fiber Drawing

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Tellurite glasses are important as a host of Er³⁺ ions because of their good solubility and because they present broadband optical gain compared with Er³⁺-doped silica, with the potential 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 like 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 Bi₂O₃ content can be used to control the refractive index of clad and core glasses. Single-mode and multi-mode Er³⁺-doped optical fibers were produced by the rod-in-tube method using highly homogeneous TeO₂–ZnO–Li₂O–Bi₂O₃–CsCl glasses.

I. Introduction

TELLURITE glass optical fibers are important for telecommunications because the Er³⁺ ion fluorescence bandwidth at 1550 nm in this host is much broader than in other glasses at the same time as the solubility limit for the rare earth is much higher.^{1,2} This means that it can be doped up to 70 000 p.p.m., allowing higher gain per unit length.³ This fact can be understood considering that Er₂O₃ is a network intermediate/modifier and not only a dopant in this kind of glass. The glass could even be called TeO₂–Er₂O₃ glass. Used in optical amplifiers, these fibers should show broadband optical amplification for wavelength division multiplexing systems, increasing the number of wavelengths of the optical channels from those of the usual Er³⁺-doped silica fibers.^{3,4} Moreover, due to the higher doping level and attenuation, these devices should require only a few centimeters of fiber length, instead of the usual tens of meter scale length that has been used up to now.^{5–7}

However, optical fiber production with this glass has been a challenge mainly due to its low glass stability range (GSR), which leads to crystallization processes at the moment of optical fiber drawing. Two other problems one has to face are how to control the difference in the 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 TeO₂–ZnO–Na₂O–Er₂O₃ and TeO₂–WO₃–Er₂O₃ families have generated international patents^{8,9} and use the Bi₂O₃ content to control the core/clad refractive index and viscosity.

The aim of this paper is to show that the 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 Er³⁺-doped optical amplifiers. To show this, we present the thermo-physical results obtained with bulk TeO₂–ZnO–Li₂O–Bi₂O₃–CsCl (TeZnLiBiCsCl) glass samples and the Er³⁺-doped optical fiber produced with them by the rod-in-tube method.

II. Experimental Procedure

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 chemical composition of the synthesized TeZnLiBiCsCl glasses was evaluated by energy dispersive X-ray spectroscopy (EDX) microanalysis in a JEOL (Tokyo, Japan) JSM 6360-LV scanning electron microscope coupled to a Noran System (Waltham, MA) SIX Model 6714A microanalyzer (operating with a beam energy of 20 kV), X-ray fluorescence (XRF) spectroscopy (EDX 700, Shimadzu, Tokyo, Japan) and by an ion selective electrode potentiometric method. For the last analysis, the TeZnLiBiCsCl-d glass sample was dissolved in 75 mL of 2.0 mol/L aqueous HNO₃ solution at 298 K.

The non-crystallinity of the samples was confirmed by X-ray diffraction analysis using CuK α radiation with a Shimadzu XD3A diffractometer. Typical temperatures related to glass stability: T_g (glass transition temperature), T_x (onset of crystallization temperature), and T_m (melting temperature) were measured by differential thermal analyses (DTA, TA-50WS, Shimadzu), while T_d (softening dilatometric point) and α (thermal expansion coefficient) were measured by thermomechanical analyses (TMA, TA 50WS, Shimadzu). The DTA measurements were performed with both powdered (particle diameter around 64 μ m) and bulk glass samples at a heating rate of 10 K/min under an argon atmosphere (20 mL/min). 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

D. Johnson—contributing editor

Manuscript No. 22265. Received September 18, 2006; approved February 12, 2007.

This work was financially supported by FAPESP and CNPq.

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Table I. Nominal Composition of the TeZnLiBiCsCl Glass Systems With Different Concentrations of CsCl, all Doped With 10 000 p.p.m. of Erbium

Sample code	Nominal composition (mol%)				
	TeO ₂	ZnO	Li ₂ O	Bi ₂ O ₃	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

samples. A Metricon model 2010 Prism Coupler instrument (Pennington, NJ), with index accuracy of 0.001, was used.

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 silica tubes with different diameters with a vacuum pump. The tellurite glasses emerge from the silica tube during the cooling process due to their very different expansion coefficients. The cladding tube composition was 68.5TeO₂-15.5ZnO-5Li₂O-1.5Bi₂O₃-9.5CsCl (mol%), and the 0.3 mm rod for the core had a 68TeO₂-15.5ZnO-5Li₂O-2Bi₂O₃-9.5CsCl (mol%) glass composition doped with 10 000 p.p.m. erbium. Both glasses, the rod and the tube, received a 2-h thermal treatment at 513 K.

A 125 μm outer diameter and 35 μm core diameter multimode optical fiber and a 125 μm outer diameter and 12 μm core diameter single-mode optical fiber were drawn with this clad-core system using a Heathway fiber-drawing tower (Wolverton Mill, U.K.) at a 2.3 m/min drawing speed. The Bi₂O₃ content was used to control the clad-core refractive index differences and to assure single-mode operation. The light guided by an optical fiber will be single mode when $V \leq 2.405$, where $V = (2\pi a/\lambda)NA$ is the optical fiber V parameter, a = fiber core radius, λ = vacuum wavelength, and $NA = \sqrt{n_{\text{core}}^2 - n_{\text{clad}}^2} \approx \sqrt{2n_{\text{clad}}\Delta n}$ is the fiber numerical aperture.¹⁰ The optical fiber attenuation measurement was performed by the cut-back method. For this purpose, a tungsten-halogen lamp (Oriel, Leatherhead, U.K.) white light was coupled at one fiber end with a 0.35- NA objective lens, collected at the other end with a multimode (50-μm core) silica fiber coupled to an optical spectrum analyzer.

III. Results

The EDX/XRF spectrum of the TeZnLiBiCsCl-d glass sample (Fig. 1) is representative of the other glass samples and it confirms the presence of Cs ($L_{\alpha 1}$ 4.286 keV) and Cl ($K_{\alpha 1}$ 2.622 keV) in the synthesized TeZnLiBiCsCl glasses. Although it is a semi-quantitative technique, it was found that the composition change due to vaporization was limited¹¹ (the loss of Cl and Cs was <6% in weight for all samples). Similar results were also reported by Ding *et al.*¹² The Cl content, for the glass sample evaluated by the selective-ion electrode potentiometric method,

Table II. Nominal Composition of the TeZnLiBiCsCl Glass Systems With Different Concentrations of Bi₂O₃, all Doped With 10 000 p.p.m. of Er₂O₃

Sample code	Nominal composition (mol%)				
	TeO ₂	ZnO	Li ₂ O	Bi ₂ O ₃	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

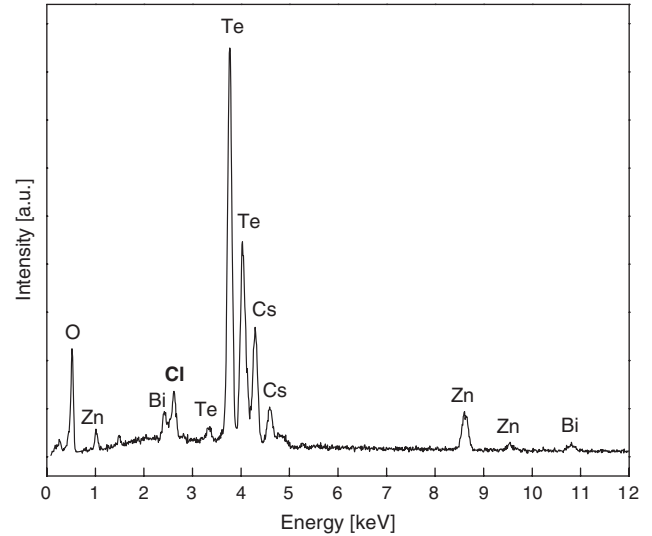


Fig. 1. Energy dispersive X-ray spectroscopy/X-ray fluorescence spectrum of the TeZnLiBiCsCl-d glass system.

is equal to 293.3 mg Cl/L per gram of the TeZnLiBiCsCl-d glass sample, while the nominal content is 305.7 mg Cl/L per gram of glass. The deviation of nominal composition was 4% in weight, corroborating the EDX/XRF data and previously reported data.^{11,12} Thus, the sample compositions are expressed as nominal compositions.

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

Figure 2 shows the DTA curves for powdered TeZnLiBiCsCl glasses with different CsCl contents, 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 $Q = (a+bT+cT^2) Q_m$, 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. The dashed lines were drawn just to guide the eyes for the enhanced 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.^{13,14} The third and fourth events are related to T_c and T_m , respectively.

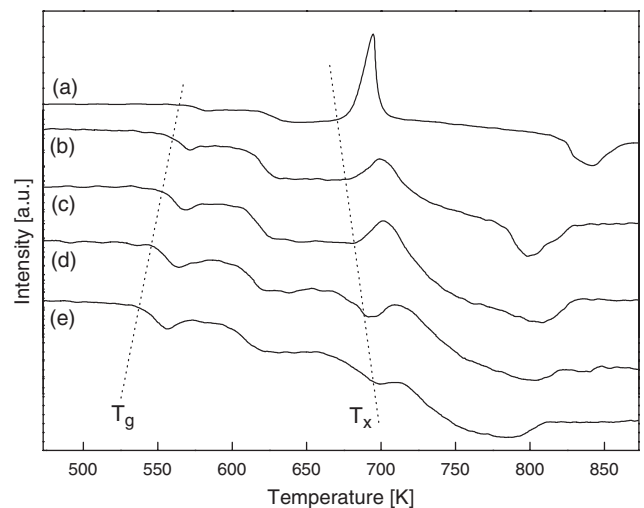


Fig. 2. Differential thermal analyses curves of the TeZnLiBiCsCl glass systems with different concentrations of CsCl.

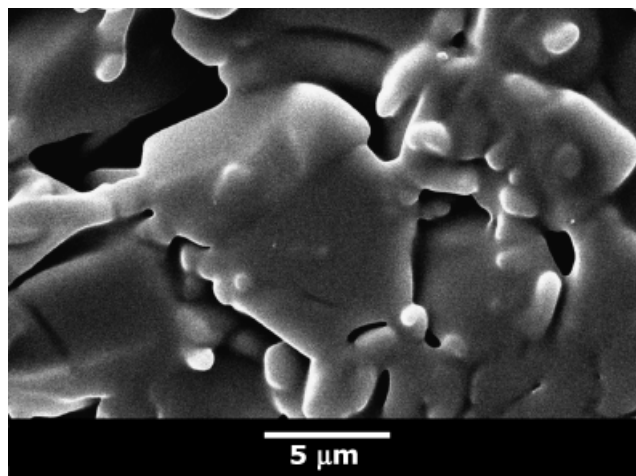


Fig. 3. Scanning electron microscopy micrograph of a compacted powdered TeZnLiBiCsCl glass [sample Fig. 1(c)] after thermal treatment at 621 K for 10 min.

In glasses, sintering takes place by the viscous flow of a glass phase and the densification phenomena occur by coalescence process, which start with the formation of necks between particles.¹³ To prove that the second thermal event observed in the DTA curve is related to sintering and not related to some other phenomenon such as a phase separation or a second T_g , powdered TeZnLiBiCsCl glass samples (149- μm mesh) were compacted and subjected to a thermal treatment at 621 K for 10 min. The sample surface was analyzed by scanning electron microscopy (SEM). The SEM image (Fig. 3) 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 GSR, $GSR = T_x - T_g$, and the Hrubý number, $H_r = (T_x - T_g)/(T_m - T_x)$,¹⁵ shown in Table III. The T_d and α are plotted as a function of the CsCl content in Fig. 4. The optical fiber can be produced when the core thermal expansion coefficient is similar to that of 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 5 shows the values for the core refractive index, n , as a function of the Bi_2O_3 content for the 632.8, 1305.4, and 1536 nm wavelengths. The optical fiber numerical aperture $NA = 0.09$, extracted from these data, is used to calculate core radius of $a = 6 \mu\text{m}$ to produce a single-mode optical fiber with the V parameter, $V = 2.2$, at 1536 nm.

For the multi-mode fiber, this parameter is $V = 6.4$, also at 1536 nm. In Fig. 6(a), the (i) curve shows the tungsten-halogen lamp spectrum collected directly by the multimode silica fiber; (ii), (iii), and (iv) curves show the transmitted intensity after passing through 37-, 57-, and 77-cm lengths of the fibers, respectively. From these curves, the attenuation spectrum of TeZnLiBiCsCl-d fiber was obtained and is shown in Fig. 6(b). The transmission window obtained for the TeZnLiBiCsCl-d fiber was between 540 and 1750 nm. The attenuation minimum value obtained was 9 dB/m for the 1300 nm wavelength. Figure 6(b)

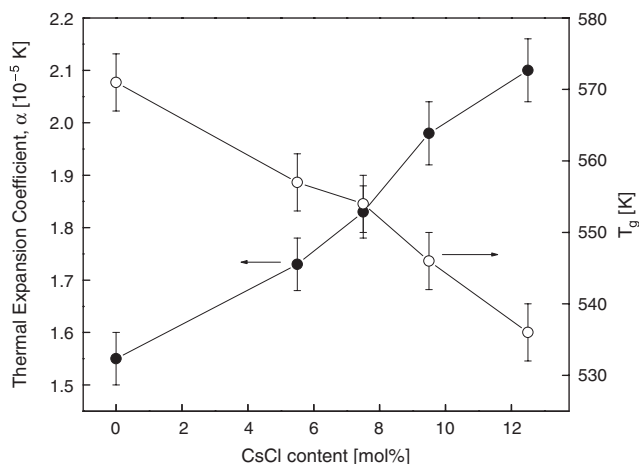


Fig. 4. Variation of the α and T_g in the TeZnLiBiCsCl glass systems with different concentrations of CsCl.

Table IV. α , n , and T_g of Both Cladding and Core of Optical Fibers Fabricated by the Rod-In-Tube Method

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

also shows the characteristic absorption bands of Er^{3+} at 660 nm ($^4\text{F}_{9/2}$), 800 nm ($^4\text{I}_{9/2}$), 980 nm ($^4\text{I}_{11/2}$), and 1540 nm ($^4\text{I}_{13/2}$).

IV. Discussions

The DTA curves of Fig. 2 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%, increasing the GSR of this glass from 378 to 433 K. The GSR increase with the CsCl content can be explained considering the structure of tellurite glasses.^{16–21} 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 electronegativity is strong enough to replace an 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, retaining 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, α 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. This is similar to heavy-metal oxide glasses where the network modifier acts as a network depolymerizer.^{22,23}

The H_r number for all glass compositions, shown in Table III, is >0.1 and some are larger than one. According to Hrubý,¹⁵ glasses with $H_r < 0.1$ are difficult to prepare and require rigorous control of the experimental conditions; glasses with $H_r = 0.5$ can be prepared easily. Although Hrubý attributed H_r numbers

Table III. T_g , T_x , T_m , T_d , α , GSR, and H_r for TeZnLiBiCsCl Glass Systems With Different Concentrations of CsCl

Code sample [†]	$T_g \pm 1$ (K)	$T_x \pm 1$ (K)	$T_m \pm 1$ (K)	GSR ± 1 (K)	H_r	$T_d \pm 1$ (K)	α (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 Fig. 1. GSR, glass stability range; DTA, differential thermal analyses.

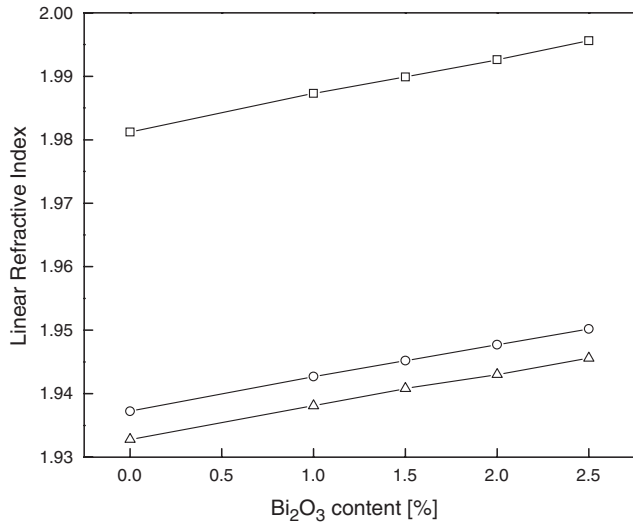


Fig. 5. Refractive indices (n) of TeZnLiBiCsCl glass systems with different concentrations of Bi₂O₃.

larger than one to high-molecular polymer-type glasses,¹⁵ our results show a depolymerization of the vitreous network.

The lack of bubbles, crystallized particles, and striations shows a good glass for optical fiber guiding purposes. The

clad-core refractive index step can be controlled by the Bi₂O₃ 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 Bi₂O₃ content of the core and clad at 0.5 mol%. The optical fiber NA can be obtained from n versus the Bi₂O₃ content curve and it can be used to calculate the core diameter, to produce a single-mode optical fiber. For the $NA = 0.09$ and a 12- μm 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.²⁴

V. Conclusion

We have shown that the potential applications of tellurite glasses for broadband optical amplifiers can be amplified by increasing their GSRs to produce better optical fibers. We also showed 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 $(78-x)\text{TeO}_2-15.5\text{ZnO}-5\text{Li}_2\text{O}-1.5\text{Bi}_2\text{O}_3-x\text{CsCl}$ (mol%) and $(70-x)\text{TeO}_2-15.5\text{ZnO}-5\text{Li}_2\text{O}-x\text{Bi}_2\text{O}_3-9.5\text{CsCl}$ (mol%) glasses and investigated the role of the CsCl in their GSR. We observed that CsCl acts like 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, that is, the core coefficient is larger than the clad one. We also show that the Bi₂O₃ 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 Er³⁺-doped tellurite glasses.

Acknowledgments

The authors are grateful to Prof. C.H. Collins (IQ-UNICAMP, Brazil) for English revision. This is a contribution of Millennium Institute for Complex Materials (PADCT/MCT).

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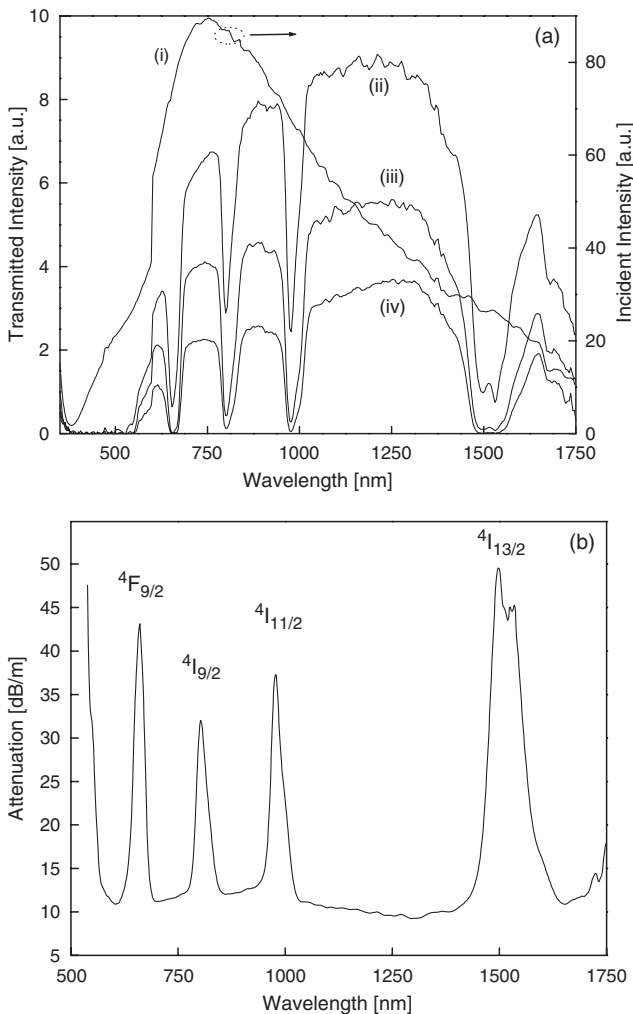


Fig. 6. (a) Tungsten-halogen lamp spectrum (i), and transmitted light intensity after passing through different length fibers, (ii), (iii), and (iv), of TeZnLiBiCsCl-d glass. (b) Attenuation curve as a function of the wavelength for optical fiber TeZnLiBiCsCl-d glass.

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