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# High-purity $TeO_2$–$WO_3$–($La_2O_3$, $Bi_2O_3$) glasses for fiber-optics

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ABSTRACT

$TeO_2$–$WO_3$, $TeO_2$–$WO_3$–$La_2O_3$ and $TeO_2$–$WO_3$–$La_2O_3$–$Bi_2O_3$ glasses were produced by high-purity oxides mixtures melting in crucibles of gold or platinum in purified oxygen atmosphere. The total content of Cu, Mn, Fe, Co and Ni impurities was not more than 0.1–2 ppm wt in glasses and below 0.1 ppm wt in the initial oxides. The hydroxyl groups absorption coefficients of the tellurite glasses at the maximum of the absorption band ($\lambda \sim 3$ μm) lay in the region of 0.01–0.001 $cm^{-1}$. Stability to crystallization characterized by $T_x - T_g$ = 150–190 °C was demonstrated for high purity $75TeO_2$–$25WO_3$ glasses by DSC-measurements. There were no thermal effects of crystallization and crystallized phases fusion in case of $La_2O_3$-containing glasses.

The optical absorption losses, measured by the laser calorimetry method at $\lambda$ = 1.06, 1.56 and 1.97 μm, did not exceed 40–120 dB/km for glass samples. The multimode optical fibers with optical losses of 50–250 dB/km at 1.2–2.2 μm were produced from high-purity $TeO_2$–$WO_3$–($La_2O_3$, $Bi_2O_3$) glasses.



## 1. Introduction

Tellurium dioxide ($TeO_2$) based glasses are transparent in the range of 0.4–6 μm, possess highly nonlinear optical properties and a high solubility of rare-earth elements. These advantages make them potentially attractive materials for active components of optical fiber communication systems and integral optics [1,2].

In accordance with literature data the optical fibers were often fabricated from multicomponent tellurite glasses based on $TeO_2$–ZnO system containing $Na_2O$, $Bi_2O_3$, $GeO_2$, $Li_2O$. For instance, single mode tellurite fibers of $Na_2O$–ZnO–$TeO_2$ glasses were made in [3] and [4] with optical losses 1.3–6 dB/m (near IR-range) and 0.24–0.7 dB/m at 1550 nm, respectively. The attenuation loss of the $TeO_2$–$GeO_2$–ZnO–$Na_2O$–$Y_2O_3$ fiber from [5] was 1.92 dB/m at 1.31 μm. The absorption of transition metals and of hydroxyl groups impurities together with scattering on inhomogeneities are the main factors determining the optical losses of tellurite glasses and fibers in IR–range.

However, the effect of purity of the initial oxides and glasses on parameters of the optical fibers fabricated on their basis is actually not considered in publications and demands special investigation.

Binary $TeO_2$–ZnO glasses have a low stability to crystallization and ($T_x - T_g$) parameter is 70–100 °C [6]. Addition of modifying components makes it possible to improve this value; however, even in this case the thermograms of DSC-analysis (10 °C/min) comprise the thermal effects of crystallization and melting of crystalline phases [4]. Crystallization can be the main obstacle to fabrication of optical fibers with low optical losses.

In comparison with them the tungstate–tellurite glasses have the advantages of higher phonon energy, higher softening point, and a significantly broader emission at 1.5 μm promising a larger gain bandwidth [7].

Stability to crystallization of this binary glass itself is not sufficient for high quality fibers fabrication either and ($T_x - T_g$) parameter is 100–130 °C [8]. Addition of $La_2O_3$ increases stability of the glasses to crystallization. Modified tungstate–tellurite glasses seem to have a great potential for fiber-optics applications.

The aims of the present work are the preparation of pure and homogeneous tungstate–tellurite glasses, investigation of their properties and development of technique for multimode optical fibers with low optical losses production.

## 2. Experimental

### 2.1. Experimental procedure

The tungstate–tellurite glasses were produced by the oxides mixture melting in gold or platinum crucible in the purified oxygen atmosphere inside the silica glass reactor.

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The compositions (mol%) of glasses prepared and the corresponding abbreviations are as follows:

$$75TeO_2 - 25WO_3 (TW),\ 69TeO_2 - 23WO_3 - 8La_2O_3\ (TWL),$$

$$67.7TeO_2 - 22.45WO_3 - 7.85La_2O_3 - 2Bi_2O_3\ (TWLB).$$

Bismuth oxide was added to the butch to increase the refractive index of glasses.

High-purity tellurium dioxide, purified by vacuum distillation [9], and the commercially available oxides of tungsten, lanthanum and bismuth of superpurity grade were used. A fluorinating chemical reagent was used for production of samples with ultra-low content of hydroxyl groups. The total content of impurities of 3d-transition metals in each of the initial oxides was less than 0.1 ppm wt by the method of chemical–atomic-emission analysis [10,11] and in the glasses it was not more than 0.1–2 ppm wt. The level of impurities of silicon, platinum (or gold) concentration in glasses, produced by melting in platinum (or gold) crucible inside silica glass chamber, is high (2–100 ppm wt). However, these impurities in tellurite glasses do not have absorption bands in the near IR-range and do not have a pronounced effect on optical losses. The content of actively absorbent in the near IR-range rare-earth elements in the glasses was less than the detection limit of the laser mass spectrometry method (<1–2 ppm wt).

The set-up for production of dry glasses provides preliminary batch mixture drying in the flow of purified oxygen or in vacuum (up to $10^{-3}$ mm Hg), melting and formation of samples with the required geometry.

Glasses were melted at 800 °C up to attaining the concentration of water vapors in oxygen leaving the reactor of $\sim 5 \times 10^{-5}$ mol% (the dew point is about −80 °C). Then the melt was poured into silica glass tubes. Further the glasses were annealed and mechanically treated by grinding and polishing for subsequent investigations.

### 2.2. Methods

IR spectra of samples were registered by IR Prestige-21 Fourier spectrometer of Shimadzu Company. Absorption coefficient spectra were calculated from transmission spectra by the Beer–Lambert–Bouguer law equation: the absorption coefficient $\alpha = -\ln(I/I_0)/x$. The visible spectra were recorded by spectrophotometer Lambda 900. STA-409 PCLUXX instrument was used for investigations by differential scanning calorimetry at heating rates of 2.5, 5, 10 deg/min. Optical losses caused by absorption were determined by laser calorimetry method in cylindrical glass samples of 40–90 mm in length and of 8–12 mm in diameter [12]. Light scattering in glass samples was investigated by the methods of optical microscopy and laser ultramicroscopy (wavelength of probe radiation $\lambda_0 = 632.8$ nm) [13]. The minimal and maximal concentrations of individual scattering centers, defined by single-particle account, were $10^2$ and $10^{10}$ cm$^{-3}$, respectively. The level of integral scattering at higher concentration was determined at right angles with respect to scattering in the reference sample of pure benzene or quartz glass: $R_\perp/R_{\perp 0} = C(n/n_0)^2$ ($R_\perp$, $R_{\perp 0}$ and $n$, $n_0$ are the Rayleigh scattering coefficients and refractive indexes of glass and reference sample, respectively; $C$ is the ratio of luminance of laser beam in glass to its luminance in the standard). The multimode optical fibers were produced by single and double-crucible method with drawing rate 3 m/min.

## 3. Results and discussion

### 3.1. Visible and IR spectroscopy of glasses

Transmission spectra in the wavelength region of 400–800 nm of high-purity tellurite glass samples are represented in Fig. 1. The data, shown in the picture, correspond to the specimens of 1.5–2 mm thick differed in composition and in crucible material (gold or platinum).

Tungstate–tellurite glasses, produced from high-purity initial oxides by melting in crucible, are characterized by high transparency in the visible range from ~450 nm. The difference in curves shape near ~500 nm can be noted and transmission of samples, produced in platinum crucible, is lower in this range. We explain it by absorption of the dissolved platinum present in concentration of 50–100 ppm wt according to the data of atomic-emission analysis. Characteristic absorption bands of other impurities are not observed in the visible range for these samples.

Fig. 2 gives the absorption spectra near the multiphonon edge (a) and the absorption maximum at 1890 cm$^{-1}$ dependence on $WO_3$ content in glasses for 1.5 mm thick samples (b). The transparency range extends up to ~5 μm for TW, TWL and TWLB glasses (Fig. 2a). Position of the 1890 cm$^{-1}$ band maxima and its intensity (Fig. 2b) are related with tungsten oxide content of the studied glasses.

The band at 1790 cm$^{-1}$ in the absorption spectra is differently interpreted by various authors. For instance, the author of [14] relates the absorption bands at 1770 and 1870 cm$^{-1}$ to the first overtone of asymmetric vibrations of $WO_6$ groups and to the first overtone of symmetric vibrations of $WO_4$ groups, respectively. However, according to [15] the $WO_4$ groups are instable in tellurite surroundings and cannot be present in glasses in perceptible amounts. In our opinion the band near 1890 cm$^{-1}$ is mostly due to O═W overtone vibrations in single and pair centers of O═$WO_5$ and the band near 1790 cm$^{-1}$ is probably due to combination of O═W and W–O–W vibrations in the pairs of O = $WO_5$ single centers.

The technique for production of glasses inside silica chamber in the flow of dry oxygen makes it possible to attain low content of hydroxyl groups in the glasses (Fig. 3). The form and location of hydroxyl band are similar for all glass compositions. The maximum of absorption coefficient is 0.006–0.012 cm$^{-1}$ for glasses produced in the flow of dry oxygen and up to 0.001 cm$^{-1}$ in case the chemical reagent is additionally used. This is the lowest values of literature data.

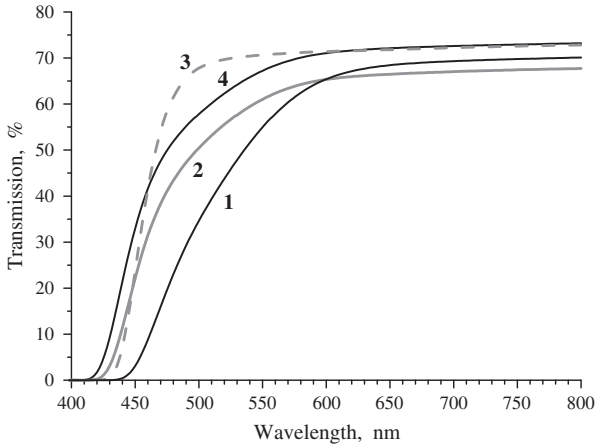


**Fig. 1.** Visible region transmission spectra of 1.5–2 mm thick tungstate–tellurite glass samples prepared in gold or platinum crucible: 1 – TW (Pt crucible), 2 – TWL (Pt crucible), 3 – TWL (Au crucible), 4 – TWLB (Pt crucible).