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GLASSES OF $TeO_2 – WO_3$ AND $TeO_2 – WO_3 – La_2O_3$ SYSTEMS FOR FIBER OPTICS

M. F. Churbanov*, G. E. Snopatin, E. V. Zorin, S. V. Smetanin, E. M. Dianov[a], V. G. Plotnichenko[a], V. V. Koltashev[a], E. B. Kryukova[a], I. A. Grishin[b], G. G. Butsin[b]

Institute of Chemistry of High-Purity Substances of RAS, 49 Tropinin Str, 603950, Nizhny Novgorod, GSP-75, Russia
[a]Fiber Optics Research Center at the A. M. Prokhorov General Physics Institute of RAS, 38 Vavilov Str, 119991, Moscow, Russia
[b]Nizhni Novgorod State University, 23 Gagarin Ave., Nizhny Novgorod, Russia

Tellurite glasses of $(TeO_2)_{0.8}(WO_3)_{0.2}$ and $(TeO_2)_{0.7}(WO_3)_{0.2}(La_2O_3)_{0.1}$ are produced by melting mixtures of respective oxides. Some properties of produced glasses essential for application in fiber optics are investigated. The best glass samples contain 0.5 – 1.0 ppm of OH groups, no more than 0.5 ppm wt. of transition metal impurities, less than 5×10^3 cm^{-3} of heterophase scattering inclusions with a diameter 0.05-0.09 μm. The kinetics of glass crystallization is studied within 380-480^{0}C. A set of properties of glasses with the aforesaid compositions makes them applicable for optical fiber production, as is proved by experiments with fiber drawing from $(TeO_2)_{0.8}(WO_3)_{0.2}$ glass by double crucible method.

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1. Introduction

Recently an increasing attention of the researchers has been paid to the TeO_2-based glasses. Due to their strong nonlinear properties and an opportunity of doping with high concentrations of rare-earth elements, these glasses are now considered to be one of the most perspective materials for the development of high-performance laser sources, amplifiers and converters of radiation for visible, near and middle IR spectral ranges. Thus the feasibility of using active elements from these glasses both in conventional and fiber forms is shown, for example, in [1 – 4]. Large second-order optical non-linearity of tellurite glasses is also demonstrated [3]. Wideband amplifiers based on stimulated Raman scattering are thought to be one of the promising trends of tellurite glass application. A tellurite fiber amplifier has been developed with a 160 nm spectral band (from 1490 to 1650 nm) and a gain coefficient of 10 dB [4].

Information on tellurite glass fiber is given in papers [1 – 5]. A $TeO_2 – ZnO – Na_2O$ glass fiber with optical losses less than 1 dB/m has been made by rod-in-tube method [1]. Optical fibers used in [4] had minimum loss of 20.4 dB/km at 1560 nm. Seddon et al. have reported on fabrication of fluorotellurite fibers with optical losses lower than 5 dB/m in 0.75 – 2.75 μm spectral region. The glass composition is $(TeO_2)_{0.7}(Na_2O)_{0.1}(ZnF_2)_{0.2}$ [5].

Glasses of $TeO_2 – WO_3$ (TWO), $TeO_2 – WO_3 – La_2O_3$ (TWLO) and some other systems may be considered as perspective materials for fiber optics. At the same time, literature data on purity, optical and thermo-mechanical glass properties are poor. Preparation of pure and homogeneous glasses necessary for fiber fabrication and investigation of their properties are the aim of the present work.

* Corresponding author: yurin@ihps.nnov.ru

2. Experimental

Tellurite glasses of different compositions were produced by melting oxide mixtures of a given composition in platinum crucible at 800°C with a subsequent solidification of glass-forming melt. Three variants of melt solidification were used. In the first one the melt was poured into a metal form heated up to T_g. After cooling the samples had the form of (3-5) ×25×25 mm^3 plates. The second way was rod drawing from the melt. The rod diameter and length were 8-14 mm and 10-15 cm, respectively. The third variant implied melt solidification directly in the crucible in the switched-off furnace mode. The melt cooling rate was 4-6 K/min. The samples had 20-50 mm diameter and 60- 90 mm height.

The oxides used for preparation of glass-forming melts were qualified as 'pure', 'pure for analysis', 'chemically pure'. The content of the main glass components was determined by electron-probe microanalysis (EPMA). Methods of laser mass-spectrometry and emission spectroscopy were used for determination of metallic impurities in glasses. The OH-group content was found by measuring the transmission spectra of glasses on IR Fourier spectrometer Bruker IFS-113v.

Table 1. Impurity content in $(TeO_2)_{0.8}(WO_3)_{0.2}$ and $(TeO_2)_{0.7}(WO_3)_{0.2}(La_2O_3)_{0.1}$ glasses.

Impurity	Content, ppm wt.		
	$(TeO_2)_{0.8}(WO_3)_{0.2}$ *		$(TeO_2)_{0.7}(WO_3)_{0.2}(La_2O_3)_{0.1}$**
Si	10	10	180
Al	3	0.06	200
Cu	0.5	0.01	< 3
Ag	2	0.002	3.7
Mn	0.5	0.003	1.1
Ni	0.2	<0.03	0.9
Fe	0.5	0.2	28
Cr	30	≤0.03	1.9
Ca	2	1	11
Zn	20	<2	9
Mg	6	2	15
Bi	0.3	50	< 4
Pb	3	0.3	2.9
Pt	–	50	90

* - determined by emission spectroscopy, ** - determined by laser mass-spectroscopy.

Laser ultramicroscopy was used to determine the size and content of heterogeneous inclusions (scattering particles) in the bulk samples of tellurite glasses. The measuring technique is described in [6]. The content of air bubbles and TeO_2 crystallites with a minimal diameter of 0.03 μm and 0.09 μm, respectively, can be determined by this method within 2×10^3 - 5×10^7 cm^{-3}. Crystallite nucleation and crystal growth rates were measured at isothermal heating near T_g. The crystal content and size in the glass bulk were determined as a function of annealing time at a given temperature. The details of measurements and resultant treatment procedures are similar to those given in [7], as applied to homogeneous crystallization of fluoride glasses. Intensive surface crystallization of TWO glasses is revealed above the deformation temperature T_d. The surface boundary between a continuous crystalline phase and glass was observed by optical microscopy. The measurement of crystalline layer depth as a function of isothermal treatment duration permitted to evaluate the crystal growth rate at heterogeneous crystallization.

Table 2. Size and content of scattering particles in tellurite glasses.

Glass	Method of melt solidification*	Particle size, μm**	Particle content, $cm^{-3} \cdot 10^{-6}$
$(TeO_2)_{0.7}(WO_3)_{0.2}(La_2O_3)_{0.1}$	I	0.08 – 0.17	2
	II	0.09 – 0.14	0.2
	III	0.04 – 0.07	0.08
$(TeO_2)_{0.8}(WO_3)_{0.2}$	I	0.05 – 0.17	0.75
	III	≥ 0.05	< 0.005

* I – pouring into a mould, II – rod drawing from the melt, III – in crucible at a switch-off furnace mode;
** Scattering particles are considered to be air bubbles.

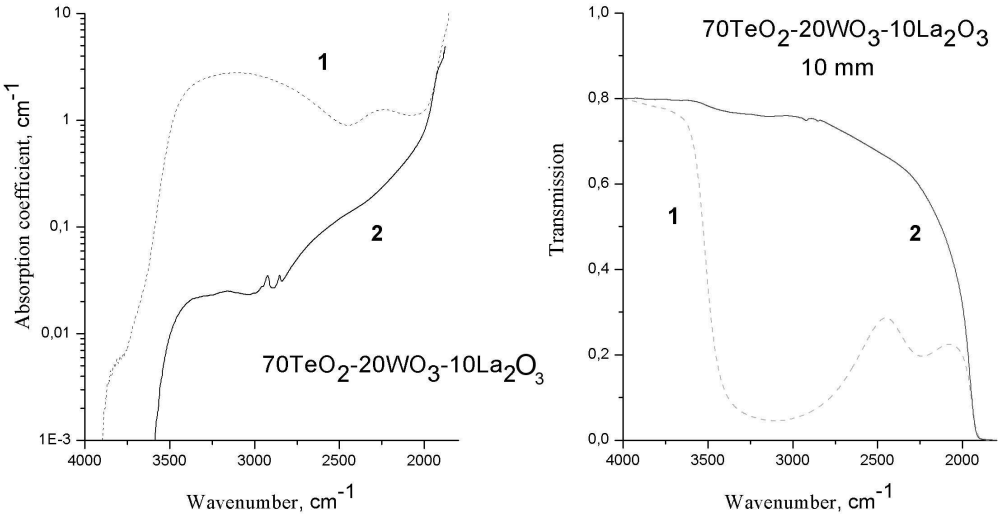
Raman spectra were measured on a Triple Raman Spectrograph T-64000 (Jobin Yvon) using macrochamber in a scattering configuration at a 90° angle. Argon laser Stabilite 2017 (Spectra Physics) was used at a 514.5 nm wavelength as an exciting radiation. A detailed description of spectrum measurement and processing is given in [8].

Optical fibers from $TeO_2 – WO_3$ glasses were fabricated by double-crucible method. Fiber was drawn at a melting temperature of 420 °C by a technique similar to that used for chalcogenide glass fiber production [9]. Optical fiber losses were measured by a standard two-point method. Mechanical fiber strength was determined by two-point bending between parallel plates at 20°C in air [9].

3. Results

$(TeO_2)_{0.8}(WO_3)_{0.2}$ and $(TeO_2)_{0.7}(WO_3)_{0.2}(La_2O_3)_{0.1}$ glasses were chosen as the main objects for tests and property investigation during fiber production. As EPMA showed, the difference between glass and charge compositions caused by TeO_2 evaporation was not higher than 1 at. %.

In Table 1 the results of emission spectroscopy and laser mass-spectroscopy analysis of tellurite glasses are presented. Fig. 1 demonstrates the transmission and absorption spectra of the bulk tellurite glass samples, where an additional procedure of the glass-forming melt treatment was used in sample 2 preparation to reduce the OH-group content.



a) b)

Fig. 1. Absorption (a) and transmission (b) spectra of TWO glasses. 1,2 – samples prepared without and with additional treatment for the OH-group removal from glass, respectively.

The data on microhomogeneity of glasses prepared by different melt solidification processes are given in Table 2. As is seen, the microinhomogeneity concentration ranges from 8×10^4 to 2×10^6 cm^{-3}. The estimation accuracy of particle concentration, resulting from repeated measurements on the same sampling volume, is 18% at a 95% confidence level.

Fig. 2 shows the change in crystal content and size in the $(TeO_2)_{0.7}(WO_3)_{0.2}(La_2O_3)_{0.1}$ glass bulk during the isothermal heating at 430°C. The glass samples used in this experiment were prepared by method I (see Table 2).

Fig. 3 presents the experimental results on temperature dependence of the nucleation rate (W), crystal growth rate (V) for homogeneous (points 1, 2) and heterogeneous (points 3) crystallizations of $(TeO_2)_{0.8}(WO_3)_{0.2}$ glass. The glass samples for investigation with initial content of heterogeneous inclusions less than 10^5 cm^{-3} were prepared by melt cooling in the crucible at a switch-off furnace mode. Arrows at points for 400 C° and 410 C° mean that the value of W and V is lower than experimental measurement limit of these parameters.

Reduced Raman spectra in VV-polarization of $x WO_3$ – (100-x) TeO_2 glass system (x varies from 12.5 to 24.8 mol. %) are presented in Fig. 4. Intensity of a wide Raman band with a shift at 600 - 800 cm^{-1} is 80 – 90 times the value for the reference SiO_2 glass.

Optical loss spectra of TWO-glass fiber fabricated by double crucible method are given in Fig. 5.

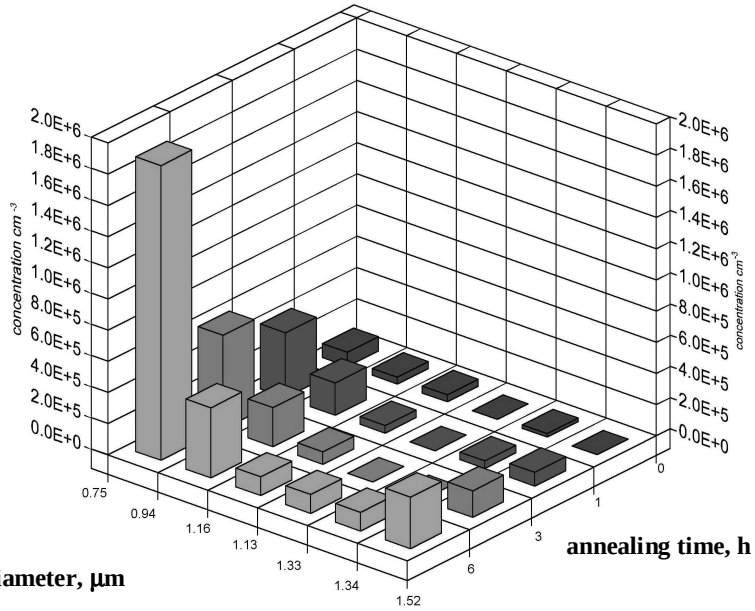


Fig. 2. Increase in size and content of scattering particles in $(TeO_2)_{0.7}(WO_3)_{0.2}(La_2O_3)_{0.1}$ glass samples after isothermal heating at 430 °C.

4. Discussion

Up to date the key requirements to glasses used for optical fiber production are as follows. These glasses should be stable to crystallization and microliquation. These processes in real time-temperature modes during the preparation of glass and its subsequent drawing into optical fibers should not lead to a change in its target properties.

The properties of substances used as initial at glass synthesis should provide their ultrapurification from the limiting impurities up to the level necessary for the given optical fiber parameters.

The basic glass should permit the composition change providing the required values of Δn, IR and Raman scattering spectra without degradation of thermo-mechanical, crystallization and other characteristics. The nature and composition of glass, as well as the related processes during

glass production and optical fiber manufacture, should provide a high degree of purity and optical microhomogeneity of glass.

As is seen from Table 1, oxide mixtures melting in platinum crucible makes it possible to produce TWO and TWLO glasses with a sufficiently low content of transition metal impurities. Their content in glass corresponds to their content in initial oxides. The use of purified TeO_2 allows to decrease noticeably (down to $n \cdot 10^{-6}$ mass. %) the content of iron in TWO glass. The presence of platinum impurity in TWLO glass proves the contaminating effect of a crucible material. The evidence for this fact can be found in paper [10].

Hydrogen in the form of water or hydroxyl groups is the most important limiting impurity. In earlier papers [11] it was shown that the content of water in glass depended on the partial pressure of water vapors over the melt. According to [11], the extinction coefficient of water in TWO glass at a 3.17 μm wavelength is equal to 108 l/mole*cm (1.5×10^4 dB/km·ppm wt.). In the "driest" samples of our glasses the OH-group content, calculated from the absorption spectra accounting for the above-mentioned extinction coefficient value, is 0.5 – 1 ppm wt. In view of the intensity ratio for the absorption bands of OH groups at 3150 and 6700 cm^{-1} in tellurite glass [11], the absorption in TWO glass at 1.3 – 1.5 μm due to the presence of 1 ppm wt. of OH groups should be at a level of 10 dB/km.

Using the data on microinhomogeneity of investigated glasses it is possible to suppose the presence of scattering centers of different types in the samples. Optical study of highly inhomogeneous glasses has revealed paratellurite crystallites and pores.

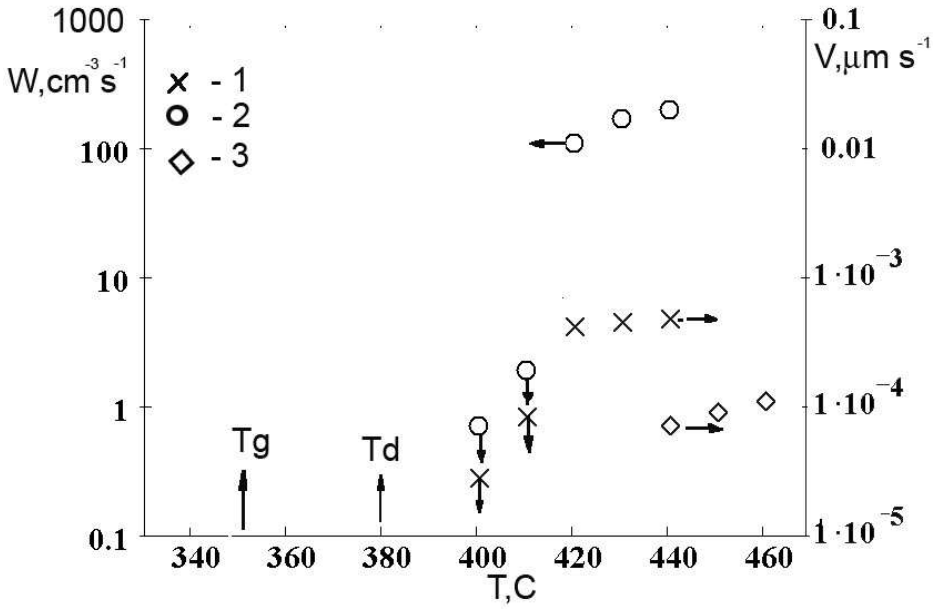


Fig. 3. Temperature dependence of nucleation rate (W) and crystal growth rate (V) for TWO glass. 1,2 — crystal growth and nucleation rates, respectively, for homogeneous crystallization. 3 — crystal growth rate for heterogeneous crystallization.

The presence of TeO_2 is confirmed by differential thermal analysis: the endothermic effect due to melting was observed at 730 °C, i.e. at the melting point of TeO_2. X-ray diffraction analysis of TWLO glass after partial crystallization during isothermal annealing confirmed the formation of TeO_2 crystallites. The presence of air bubbles in glass is a natural sequence of the melt contact with air, at melting of the oxide powder mixture, at rod drawing and at casting into metallic molds. The air dissolved or trapped in the melt is released in the form of bubbles with cooling. The amount and size of the bubbles depend on cooling process. Cooling the melts with larger amounts of dissolved

air from higher temperatures and at faster rates results in higher bubble concentrations. This explains the higher concentration of scattering centers in glasses prepared by casting into metallic molds in comparison with the samples obtained by drawing from the melt or solidified in the crucible. Fine platinum particles become trapped by the melt during the oxide mixture melting at 800 °C. Mass-spectrometric and emission spectroscopy analysis showed that the $(TeO_2)_{0.7}(WO_3)_{0.2}(La_2O_3)_{0.1}$ and $(TeO_2)_{0.8}(WO_3)_{0.2}$ glasses contained ~ 50-90 ppm wt. of Pt. Using X-ray diffraction Blanchandin et al. [10] revealed platinum and gold particles in TeO_2-WO_3 glasses prepared with platinum and gold crucibles, respectively.

It seems sufficient to note the conditions that provide highly homogeneous glasses: in $(TeO_2)_{0.8}(WO_3)_{0.2}$ glass prepared by furnace-cooling in crucible the concentration of scattering inclusions is below the detection limit of laser ultramicroscopy 5×10^3 cm^{-3}. Measurements of nucleation rate and crystal growth rate for TWO and TWLO glasses (Fig. 3) indicated their relatively high stability to crystallization in the vicinity of glass-forming and deformation temperatures. The growth of scattering centers in the bulk of glass samples annealed during several hours was not observed in experiments at temperatures of 350-420 °C and 400-520 °C for TWO and TWLO glasses, respectively.

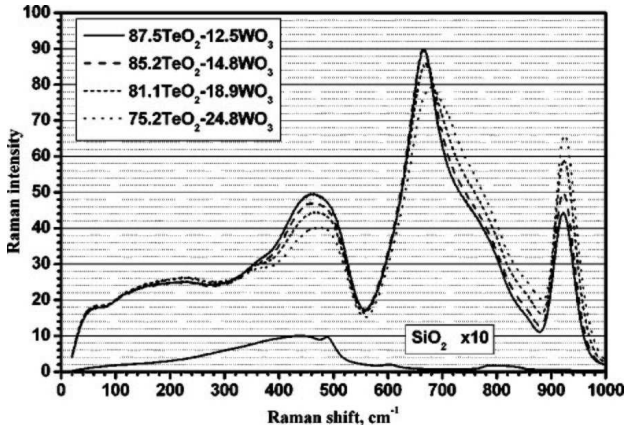


Fig. 4. Reduced Raman spectra (VV-polarization) of $x$$WO_3$ - $(100-x)$$TeO_2$ glass system.

It was also noticed that the way of melt solidification affects the crystallization ability of glass samples of the same composition. High stability is found in the samples prepared in the form of rods by drawing from the melt. In this case the glass is subjected to heat treatment for a shorter period of time. It may be assumed that the content of crystals with a diameter less than the detection limit of laser ultramicroscopy is the lowest in these samples.

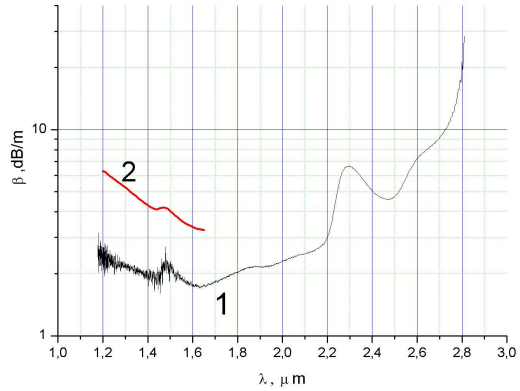


Fig. 5. Optical loss spectra of TWO glass fiber. Core glass composition:
1. $(TeO_2)_{0.6}(WO_3)_{0.285}(Bi_2O_2)_{0.125}$, 2. $(TeO_2)_{0.8}(WO_3)_{0.2}$.

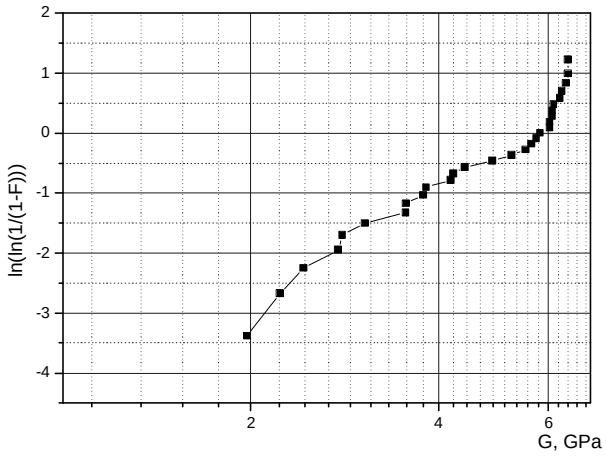


Fig. 6. Weibull plots for the bending strength of TWO glass fiber. Core and clad diameters are 26 and 350 μm, respectively.

Glass optical fibers can be prepared by extrusion, drawing from monolithic or made-up preform (the rod-in-tube method), and drawing from double crucible. The operating temperature interval for these three methods corresponds to viscosity value ranging from 10^8 to 10^4 Poise. For $(TeO_2)_{0.8}(WO_3)_{0.2}$ glass it corresponds to the temperature interval of 370-430 °C. The drawing temperature in the double-crucible method of 410-420 °C is mostly close to the crystallization temperature of ~450 °C determined by DTA measurements. The experiments on drawing from double crucible indicated the possibility to manufacture the optical fibers with the outer diameter of 150-400 μm and core/clad diameter ratio from 1:3 to 1:16. As is seen from Fig. 5, the optical losses in the fibers are high (2-5 dB/m at 1.2-2.5 μm) and are caused by a high content of impurities, mainly the OH groups and transition metals. Fig. 6 gives the Weibull distribution for bending strength of TWO optical fiber with core diameter of 26 μm and the outer diameter of 350 μm. One can see that the optical fibers have a high mechanical strength. This corresponds to a high value of the Young's modulus and agrees well with the applied method of optical fiber production. The value of the Young's modulus for TWLO glass measured by acoustic method of bending resonance was found to be equal to 61±4.2 GPa. At the same time, the double-crucible method provides a high quality of side fiber surface, as it was shown for chalcogenide glass fibers [9]. Tellurite glass fibers fabricated by double-crucible method did not contain any visible traces of crystallization. This indicates a sufficient stability of TWO glasses to crystallization and a proper choice of time-temperature modes in the process of fiber fabrication. Further progress in the development of tellurite glasses for fiber optics requires increasing their chemical and phase purity and precise measurement of properties of high-purity glasses.

5. Conclusion

The results of carried out investigations indicated the expediency in development of glasses of TeO_2-WO_3 and TeO_2-WO_3-La_2O_3 systems composition as materials for fiber optics. In this work the samples of glasses are produced with a low content (≤0.5 ppm wt.) of limiting impurities and nano-dimensional heterogeneous inclusions. The glasses are sufficiently stable to crystallization near their deformation temperature, and it permits to use the double-crucible method for fabrication of optical fibers.

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