

Production and properties of high purity glasses of $\text{TeO}_2\text{--WO}_3$, $\text{TeO}_2\text{--ZnO}$ systems

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Tellurite glasses of $\text{TeO}_2\text{--WO}_3$ and $\text{TeO}_2\text{--ZnO}$ are produced by melting mixtures of the respective oxides. Commercially available oxides were used for preparation of $\text{TeO}_2\text{--WO}_3$ glasses. $\text{TeO}_2\text{--ZnO}$ glasses have also been prepared through chemical vapour deposition from tellurium and zinc alkyl compounds in an oxyhydrogen flame. In the best glass samples, the content of metal impurities does not exceed 0.1–1 ppm wt, OH groups are at the level of 0.3–1 ppm wt, the scattering heterophase centres with diameter $\leq 100\text{--}200$ nm being less than $5 \times 10^3 \text{ cm}^{-3}$.

1. Introduction

Tellurite glasses possess a broad transmission window (0.4–6 μm) and highly nonlinear optical properties, are chemically stable, and have a high solubility limit of rare earth elements. These advantages make them potentially attractive materials for active components of optical fibre communication systems.^(1–3) A large second order optical nonlinearity of tellurite glasses has been demonstrated.⁽⁴⁾ Wideband amplifiers based on stimulated Raman scattering are thought to be one of the promising trends of tellurite glass application. A tellurite fibre amplifier has been developed with a 160 nm spectral band (from 1490 to 1650 nm) and a gain coefficient of 10 dB.⁽⁵⁾ Optical fibres used in this work had minimum loss of 20.4 dB/km at 1560 nm. A $\text{TeO}_2\text{--ZnO--Na}_2\text{O}$ glass fibre with optical losses less than 1 dB/m has been made by the rod-in-tube method.⁽⁶⁾ O'Donnell *et al* have reported the fabrication of fluorotellurite fibres (the core glass of composition is $(\text{TeO}_2)_{0.7}(\text{Na}_2\text{O})_{0.1}(\text{ZnF}_2)_{0.2}$) with optical losses 2–5 dB/m in 0.7–2.75 μm spectral region.^(6,7) A standard approach to the preparation of tellurite glasses is to melt an oxide batch in a platinum or gold crucible and, after homogenisation, to cool the melt. The purity of the resulting glass depends on the impurity concentrations in the batch components and in the gaseous environment of the melting process. The purity of commercially available oxides is, however, below the level required for advanced

optical fibre applications.

Two attractive glass forming systems are $\text{TeO}_2\text{--ZnO}$ and $\text{TeO}_2\text{--WO}_3$, which have a broad glass forming regions: 9–40 mol% ZnO and 5–35 mol% WO_3 , respectively. For the first system for both tellurium and zinc, there are sufficiently volatile metallorganic precursors (MOPs) available commercially as high purity reagents. The use of such precursors in the oxidation process results in the preparation of purer batches.

Glasses of $\text{TeO}_2\text{--ZnO}$ (TZO) and $\text{TeO}_2\text{--WO}_3$ (TWO) and some other systems may be considered as prospective materials for fibre optics. At the same time, literature data on purity, optical and thermomechanical glass properties are poor. Preparation of pure and homogeneous glasses necessary for fibre fabrication and the investigation of their properties are the aims of the present work. The goal of investigation also included the development of a technique for producing glasses with low content of impurities and heterophase inclusions, as well as the investigation of the properties of the produced glasses.

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 the glass forming melt. Three variants of melt solidification were used for $\text{TeO}_2\text{--WO}_3$ glasses. In the first one, the melt was poured into a metal form heated up to T_g . After cooling the samples had the

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Table 1. Impurity content in initial TeO_2 , WO_3 , ZnO and $(\text{TeO}_2)_{0.8}(\text{WO}_3)_{0.2}$, $(\text{TeO}_2)_{0.75}(\text{ZnO})_{0.25}$ glasses determined by emission spectroscopy

Impurity	Content, ppm wt.		$(\text{TeO}_2)_{0.8}(\text{WO}_3)_{0.2}$	TeO_2 CVD-made	ZnO CVD-made	$(\text{TeO}_2)_{0.75}(\text{ZnO})_{0.25}$
	TeO_2 'extra pure'	WO_3 'pure'				
Si	1	40	60	<1	≤1	<1
Cu	<0.08	≤0.1	≤0.1	<0.08	<0.08	<0.08
Ti	<6	<6	<6	<6	<6	<6
Al	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Mn	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cr	<1	30	7	<1	<1	<1
Ni	<0.5	<3	<3	<0.5	<0.5	<0.5
Sn	<2	<2	<2	<2	<2	<2
Ca	<10	<20	<20	<10	<10	<10
Cd	<6	<6	<6	<6	<6	<6
Fe	<0.5	1	<0.5	<0.5	<0.5	<0.5
V	<5	<5	<5	<5	<5	<5
Sb	<10	<10	<10	<10	<10	<10
Mo	≤7	<7	<7	<7	<7	<7
Ag	<0.03	<0.04	<0.04	<0.03	<0.03	<0.03
Co	<5	<5	<5	<5	<5	<5
Pt	<0.5	<0.5	10	<0.5	<0.5	50

form of $(3-5) \times 25 \times 25 \text{ mm}^3$ plates. The second way was by 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 were 30–40 mm in diameter and 20–25 mm in height.

The reagent grade qualified as 'extra pure' TeO_2 and 'pure' WO_3 were used for the preparation of glass forming TeO_2 – WO_3 melts by fusing the mixtures of oxides. Triple component glasses $(\text{TeO}_2)_{0.7}(\text{WO}_3)_{0.2}(\text{La}_2\text{O}_3)_{0.1}$ (TWLO) or $(\text{TeO}_2)_{0.6}(\text{WO}_3)_{0.28}(\text{Bi}_2\text{O}_3)_{0.12}$ (TWBO) were also made. For the preparation of TeO_2 – ZnO glass samples, TeO_2 and ZnO were obtained through chemical vapour deposition from tellurium and zinc alkyl compounds in an oxyhydrogen flame onto the lateral surface of rotating cylindrical substrates. The method for the preparation of high purity mixtures and individual Te and Zn oxides via the oxidation of $\text{Te}(\text{CH}_3)_2$ and $\text{Zn}(\text{CH}_3)_2$ in the gas phase (CVD) in detail was described previously.⁽⁸⁾ The difference between glass and charge compositions was caused only by TeO_2 evaporation and it was no higher than 0.5 at%. A dried oxygen environment was used to decrease the OH group content in the resulting glasses during preliminary thermal treatment and melting of oxide batches took place in a platinum crucible.

The content of the main glass components was determined by electron probe microanalysis (EPMA). Emission spectroscopy was used to determine the presence 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. 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 was described in Ref. 9. The content of air bubbles and TeO_2

crystallites with a minimum diameter of more than $0.03 \mu\text{m}$ and $0.09 \mu\text{m}$, respectively, can be determined by this method within 2×10^3 – $5 \times 10^7 \text{ cm}^{-3}$. Crystallite nucleation and crystal growth rates were measured on 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 Ref. 10, as were applied to homogeneous crystallisation of fluoride glasses. Intensive surface crystallisation 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 allowed us to evaluate the crystal growth rate at heterogeneous crystallisation.

Optical fibres from TeO_2 – WO_3 glasses were fabricated by the double crucible method. Fibre was drawn at a melting temperature of 420°C by a technique similar to that used for chalcogenide glass fibre production.⁽¹¹⁾ Optical fibre losses were measured by a standard two-point method. Mechanical fibre strength was determined by two-point bending between parallel plates at 20°C in air.

3. Results and discussion

The key requirements of glasses used for optical fibre production are as follows: these glasses should be stable to crystallisation and microsegregation; the nature and composition of glass, as well as the related processes during glass production and optical fibre manufacture, should provide a high degree of purity and optical microhomogeneity of glass.

The properties of substances used as starting materials for glass synthesis should allow their ul-

trapurification from the limiting impurities up to the level necessary for the given optical fibre parameters. Table 1 summarises the results of emission spectroscopy analysis of initial oxides and $(\text{TeO}_2)_{0.8}(\text{WO}_3)_{0.2}$, $(\text{TeO}_2)_{0.75}(\text{ZnO})_{0.25}$ glasses. Oxide mixtures melting in platinum crucible makes it possible to produce TWO and TZO glasses with a sufficiently low content of transition metal and other impurities. Impurity levels in glass corresponds to their content in the initial oxides. The use of CVD-prepared TeO_2 and ZnO allows to noticeably decrease the content of Cr, Cu and Si in TZO glasses lower than the detection limit. The presence of platinum impurity in both glasses proves the contaminating effect of the crucible material.

Hydrogen in the form of water or hydroxyl groups is the most important limiting impurity. Figures 1 and 2, respectively, demonstrate the transmission and absorption spectra of the bulk tellurite glass samples, where an additional procedure of the glass forming melt treatment was used.

Earlier⁽¹²⁾ it was shown that the content of water in glass depended on the partial pressure of water vapours over the melt. According to that paper, the extinction coefficient of water in tellurite glasses at a 3-17 μm wavelength (wavenumber 3150 cm^{-1}) is equal to 108 l/mole cm ($1.5 \times 10^4\text{ dB/km ppm wt}$). 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 0.3-1 ppm wt.

Using the data on microinhomogeneity of investigated glasses, it is possible to propose the presence of scattering centres of different types in the samples. 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 $2 \times 10^6\text{ cm}^{-3}$. Optical study of highly inhomogeneous glasses has revealed paratellurite crystallites and pores. X-ray diffraction analysis of TWLO glass after partial crystallisation during isothermal annealing confirmed the formation of TeO_2 crystallites. The presence of air bubbles in glass is a natural consequence of the melt being in contact with air, the melting of the oxide powder mixture, at rod drawing and at casting into metallic

Table 2. Size and content of scattering particles in $(\text{TeO}_2)_{0.8}(\text{WO}_3)_{0.2}$ and $(\text{TeO}_2)_{0.7}(\text{WO}_3)_{0.2}(\text{La}_2\text{O}_3)_{0.1}$ glasses (I – pouring into a mould, II – rod drawing from the melt, III – in crucible at a switch-off furnace mode)

Glass	Method of melt solidification	Particle size, μm^*	Particle content, $\text{cm}^{-3} \times 10^{-6}$
$(\text{TeO}_2)_{0.7}(\text{WO}_3)_{0.2}(\text{La}_2\text{O}_3)_{0.1}$	I	0.08-0.17	2
	II	0.09-0.14	0.2
	III	0.04-0.07	0.08
$(\text{TeO}_2)_{0.8}(\text{WO}_3)_{0.2}$	I	0.05-0.17	0.75
	III	0.05-0.1	<0.005

* Scattering particles are considered to be air bubbles

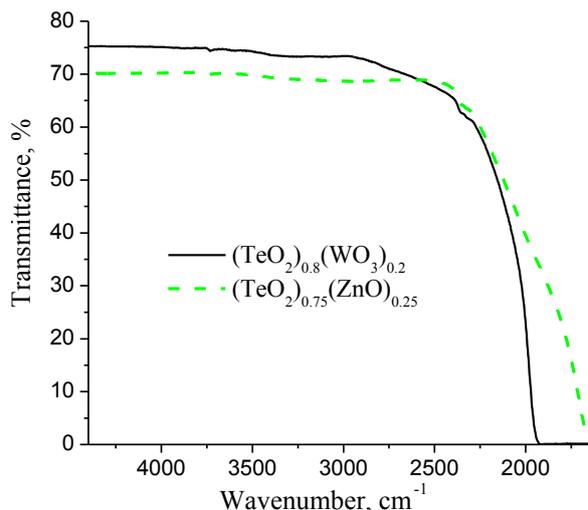


Figure. 1 Transmission spectra of tellurite glasses ($l \approx 1\text{ cm}$)

moulds. Fine platinum particles become trapped by the melt during the oxide mixture melting at 800°C . Emission spectroscopy analysis showed that the TWO, TZO and TWLO glasses contained $\sim 5\text{--}100\text{ ppm wt}$ of Pt (Table 1). Using x-ray diffraction Blanchandin *et al*⁽¹³⁾ revealed platinum and gold particles in $\text{TeO}_2\text{--WO}_3$ glasses prepared with platinum and gold crucibles, respectively.

High stability is found in the samples prepared in the form of rods drawn 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.

Glass optical fibres can be prepared by extrusion, drawing from monolithic or made-up preform (the rod-in-tube method), and drawing from a double crucible. The operating temperature interval for these three methods corresponds to viscosity value

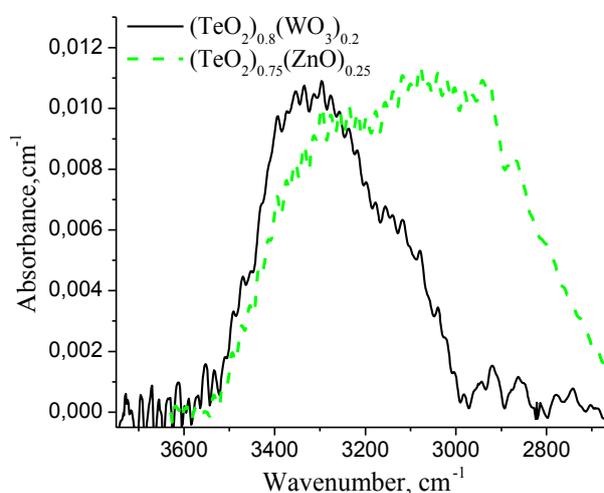


Figure 2. Absorbance of OH groups in tellurite glasses

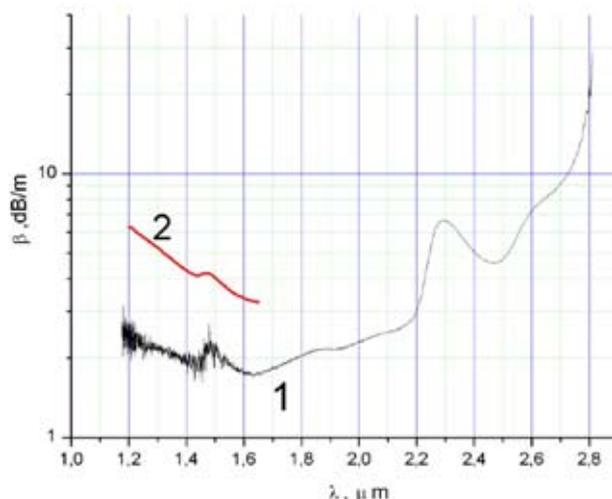


Figure 3. Optical loss spectra of TWO glass fibre. Core glass composition: 1. $(\text{TeO}_2)_{0.6}(\text{WO}_3)_{0.28}(\text{Bi}_2\text{O}_3)_{0.12}$, 2. $(\text{TeO}_2)_{0.8}(\text{WO}_3)_{0.2}$

ranging from 10^8 to 10^4 Poise. For $(\text{TeO}_2)_{0.8}(\text{WO}_3)_{0.2}$ glass this 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 crystallisation temperature of ~450°C determined by DTA measurements. The experiments on drawing from a double crucible indicated the possibility of manufacturing the optical fibres with an outer diameter of 150–400 μm and core/clad diameter ratio from 1:3 to 1:16. As it is seen from Figure 3, the optical losses in the fibres 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. Figure 4 gives the Weibull distribution for strength while bending the optical fibre with a $(\text{TeO}_2)_{0.8}(\text{WO}_3)_{0.2}$ core having of 26 μm diameter and an outer diameter of 350 μm . One can see that the optical fibres have a high mechanical strength. At the same time, the double crucible method provides a high quality of outside fibre surface, as is shown for chalcogenide glass fibres.⁽¹¹⁾ Tellurite glass fibres fabricated by the double crucible method did not contain any visible traces of crystallisation. This indicates a sufficient stability of TWO glasses to crystallisation and a proper choice of time–temperature modes in the process of fibre fabrication.

4. Conclusion

The glasses of TeO_2 – WO_3 and TeO_2 – ZnO systems have been produced by melting of oxide mixtures in a platinum crucible. Commercially available oxides have been used to prepare glass forming TeO_2 – WO_3 melts and TeO_2 – ZnO batches have been made through chemical vapour deposition from tellurium and zinc alkyl compounds in an oxyhydrogen flame. It is found in both cases that the content of metal impurities in glass is determined by the degree of purity

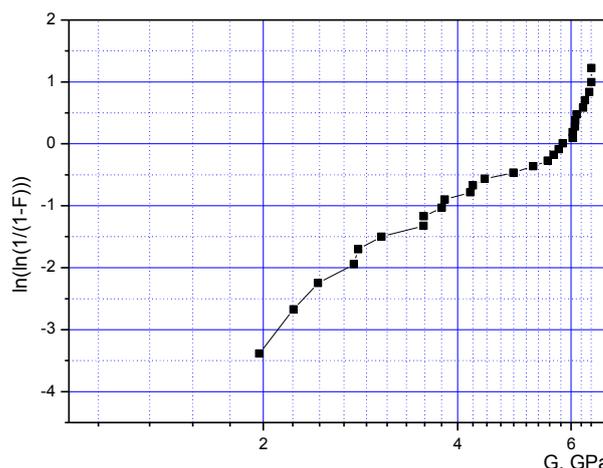


Figure 4. Weibull plots for the bending strength of TWO glass fibre. Core and clad diameters are 26 and 350 μm , respectively

of the starting oxides and does not exceed 0.1–1 ppm wt. The hydroxyl group contamination arising from the dried gaseous environment of the fusing box are at a level of 0.3–1 ppm wt, the microinhomogeneity concentration are in ranges from 8×10^4 to $2 \times 10^6 \text{ cm}^{-3}$, and in the best glass samples the scattering heterophase centres with diameter ≤ 100 –200 nm are less than $5 \times 10^3 \text{ cm}^{-3}$. The glasses are sufficiently stable to crystallisation near their deformation temperature, and this permits one to use the double crucible method for fabrication of optical fibres.

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