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Production of high-purity TeO_2-ZnO and TeO_2-WO_3 glasses with the reduced content of OH-groups

M. F. CHURBANOV*, A. N. MOISEEV, A. V. CHILYASOV, V. V. DOROFEEV, I. A. KRAEV,
M. M. LIPATOVA, T. V. KOTEREVA, E. M. DIANOV[a], V. G. PLOTNICHENKO[a], E. B. KRYUKOVA[a]
Institute of Chemistry of High-Purity Substances of RAS, N. Novgorod, Russia
[a]Optical Fiber Research Center of RAS, Moscow, Russia

The glasses of TeO_2 – ZnO and TeO_2 – WO_3 system have been produced by melting the mixture of high-purity oxides in platinum crucible in the flow of purified oxygen with subsequent cooling of the melt. The total content of the impurities of transition metals in these glasses did not exceed 1 ppm wt. The content of platinum impurity is at the level of 5-100 ppm. The effect of temperature, time of synthesis and the concentration of water in oxygen, on the content of OH-group impurities in glasses was investigated. The samples of tellurite glasses are obtained with the factor of bulk optical absorption not more than 0.002 cm^{-1} at 3.0-3.2 μm.

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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 limit of rare-earth elements. These advantages make them potentially attractive materials for active components of optical fiber communication systems and integral optics [1-3]. Theoretical estimations indicated that the tellurite glasses should have a low level of intrinsic optical losses with the minimum of 3.5×10^{-3} dB/km at 3.02 μm [4]. However, the typical experimental values for optical losses in tellurite optical fibers are substantially higher and are equal to 1000-2000 dB/km at 1.55 μm [4-6] which limit the possible application of tellurite glasses. The impurities of transition metals and of hydroxyl groups are the main factors determining the optical losses of glasses in IR-range. The effect of these impurities upon the level of optical loss has not been actually studied. With quartz and fluoride glasses as an example it was shown that the total content of the impurities of transition metals (Fe, Cr, Ni, Mn, Co, V, and Cu) in these glasses at the level of ~0.1ppm wt. led to the losses of ~10-20 dB/km at λ = 1-2 μm [7,8]. The absorption due to the impurity of OH-groups is of more significance. The concentration of hydroxyl groups of 1 ppm wt. in quartz optical fibers leads to the losses of ~ 10 000 dB/km at the wavelength of maximum OH-groups absorption 2.7 μm [9]. In papers [10,11] the absorption coefficients for OH-groups in tellurite glasses at λ = 3.1 – 3.3 μm are found which makes it possible to conclude that their content of 1 ppm mol. leads to the losses of 1000 – 2000 dB/km at this wavelength. Thus, the lowering in concentration of the impurities of metals and OH-groups is the required provision for obtaining the low optical losses in tellurite glasses.

The glasses of TeO_2 – ZnO and TeO_2 – WO_3 system are characterized by broad boundaries of glass-formation and by chemical stability. The goal of the present paper is to produce tellurite glasses of TeO_2-WO_3 and TeO_2-ZnO system with low content of the impurities of metals and hydroxyl groups.

2. Experimental

The glasses of TeO_2 – ZnO, TeO_2 – WO_3 systems in the form of bulk samples are obtained by melting the initial mixture of oxides in platinum crucible in the oxygen flow, purified from hydrocarbons and water, with subsequent cooling of the melt. A high-purity batch mixture of the given composition (20-25 mol.% ZnO), produced by gas-phase deposition of oxides from the vapors of organo-metallic compounds in the flame of hydrogen-oxygen burner [12], was used as the initial substance for production of TeO_2 – ZnO glasses. For production of TeO_2 – WO_3 glasses the high-purity TeO_2, obtained by the method of vacuum distillation [13], and WO_3, obtained by hydrolysis of tungsten hexafluoride [14], were used. To decrease the crystallization rate of tungsten-tellurite glasses the lanthanum oxide (La_2O_3) of grade 'pure' was introduced into composition of some samples. The content of impurities in the initial components for glass melting, determined by atomic-emission spectrometry, is given in Table 1.

Table 1. Results of atomic-emission and chemical spectral analysis for TeO_2 purified by vacuum distillation method, WO_3 produced by hydrolysis of tungsten hexafluoride and for TeO_2-ZnO batch mixture (25 mol.% ZnO) produced by gas-phase deposition, ppm wt.

Impurity	TeO_2	WO_3	TeO_2 - ZnO
Si	≤ 1	≤ 1	≤ 1
Cu	0.01	< 0.1	< 0.1
Ti	0.03	< 6	< 6
Al	0.03	< 0.8	< 0.8
Mn	0.006	< 0.2	< 0.2
Cr	< 1	≤ 1	< 1
Pb	0.1	< 1	< 1
Ni	< 0.03	< 3	< 0.5
Sn	< 0.008	< 2	< 2
Ca	< 0.08	< 20	< 10
Fe	0.01	< 0.5	≤ 0.5
Mg	≤ 0.05	≤ 1	< 0.1
V	< 0.04	< 5	< 5
Sb	< 0.2	< 10	< 10
Mo	≤ 7	< 7	< 7
Ag	< 0.03	< 0.04	< 0.03
Co	< 0.05	< 5	< 5
Na	< 10	< 10	≤ 10
Bi	< 0.5	< 0.5	< 0.5

Oxygen was purified from hydrocarbon impurities by passing it through the heated palladinized silica gel and from the impurity of water — by passing through molecular sieves of NaX type. The content of hydrocarbon impurities in the purified oxygen was lower than ($C_1 \div C_4$) < 0.1 mol.. The dew point of the purified oxygen was not worse than –76 ^{0}C.

Fig. 1 gives a scheme of the set-up for production of high-purity tellurite glasses with low content of hydroxyl groups. It consists of demountable quartz reactor with cooled flanges and external resistive furnace in side which the platinum crucible with the initial batch mixture was placed. After loading the initial batch mixture was heated in the residual oil-free vacuum 10^{-3} – 10^{-4} mm Hg at temperature of 500-600 ^{0}C for several hours to remove the gas-forming and volatile impurities. The mass of batch mixture is 35-50 g., the synthesis temperature is 800-850 ^{0}C, and the melting time is 1-4 hours. The glasses were produced by fast cooling of the melt removing the crucible from the hot zone.

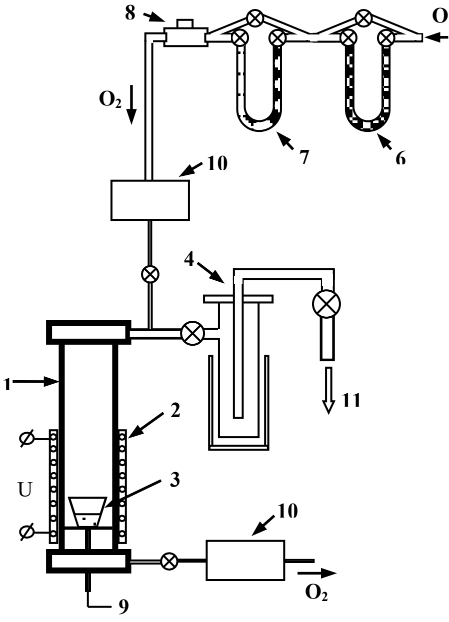

Fig. 1. Set-up for production of tellurite glasses with low content of hydroxyl groups: 1 – quartz reactor, 2 – resistive heater, 3 – crucible, 4 – trap cooled with liquid nitrogen, 5 – O_2 commercial, 6 – Pd silica gel, 7 – NaX molecular sieves, 8 – electronic flow regulator, 9 – thermocouple, 10 – IVA-8 humidity meter, 11 – turbo-molecular pump.

The water content in oxygen was controlled at the reactor output by sorption humidity indicator and by dew point direct method, i.e. by condensation of moisture on the cooled platinum surface. The content of water in oxygen over the glass melt could be changed by variation purification degree of oxygen.

The content of metal impurities in glasses was determined by the atomic-emission spectroscopy method. The content of hydroxyl groups was estimated by IR-spectroscopy method. The IR-transmission spectra of glasses are obtained by Fourier spectrometer IR Prestige-21 equipped with DLATGS detector with spectral resolution of 2 cm^{-1}.

3. Results and discussion

Table 2 gives the content of metal impurities in glasses of 0.75 TeO_2 – 0.25 ZnO and 0.78 TeO_2 – 0.22 WO_3 compositions that we produced from high-purity initial oxides. The content of all controlled impurities in glasses, except for platinum impurity, did not exceed the of detection limits of the direct spectral method. Typical content of platinum in glasses of TeO_2 – ZnO system exceeded that in TeO_2 – WO_3 glasses by several times and was at the level of 80±30 ppm and 10 ± 3 ppm, respectively. It is shown that the solubility of platinum in 0.8 TeO_2 – 0.2 WO_3 glass at 800-850 ^{0}C attained 5 ppm wt [15], i.e., the content of platinum in our glass samples is close to the limit of solubility.

Table 2. Results of direct spectral analysis for 0.8 TeO_2 - 0.2 ZnO u 0.78 TeO_2 – 0.22 WO_3 glasses (synthesis temperature 800 ºC, duration 2 hours).

Impurity	Impurity concentration, ppm wt	
	$0.8TeO_2 – 0.2ZnO$	$0.78TeO_2 – 0.22WO_3$
Si	< 1	≤ 1
Cu	< 0.1	< 0.1
Ti	< 6	< 6
Al	< 0.8	≤ 0.8
Mn	< 0.2	< 0.2
Cr	< 1	< 1
Pb	< 1	<1
Ni	< 0.5	< 0.5
Sn	< 2	< 2
Ca	< 10	< 10
Cd	< 6	< 6
Fe	≤ 0.5	< 0.5
Mg	≤ 0.1	≤ 0.1
V	< 5	< 5
Sb	< 10	< 10
Mo	< 7	≤ 7
Ag	< 0.02	≤ 0.02
Co	< 5	< 5
Bi	< 0.5	< 0.5
Pt	10	5

It is known that platinum is one of the most inert crucible material for melting the different glasses. However, in the first papers on production of tellurite glasses the effect of crucible material upon glass color was noticed which is probably connected with dissolution of crucible material in glass melt. The effect of platinum impurity upon optical losses of glasses depends upon its nature in glass matrix. The dissolved platinum does not have absorption bands in IR-range spectrum while appearance of metal particles could lead to additional scattering and absorption of light in this range. There are no data on the mechanism of entrance and on the nature of platinum impurity in tellurite glasses. Investigations, carried out for phosphate glasses [16], indicate that the form of platinum presence in glass, dissolved as ions (Pt^{4+}) or as heterophase inclusions of metal platinum, depends upon the environment under which the glasses are produced. Oxidizing environment (O_2, Cl_2 or their combination) provided the dissolved form of platinum impurity presence while air environment led to appearance of particles of metal platinum. According to the results of ultramicroscopic investigation heterophase metal inclusions with size exceeding 200 nm were not detected in our glasses. The problem on the form of platinum impurity in tellurite glasses is still should be solved.

Apart from metal impurities the optical losses in IR-range are mostly affected by the impurities of hydroxyl groups. The absorption bands, due to different content of OH-groups, in glasses of 0.78 TeO_2 – 0.22 WO_3 compositions are given in Fig. 2, and the dependence of the maximum of hydroxyl group absorption upon the pressure of water vapors over the melt during synthesis of glasses is given in Fig. 3.

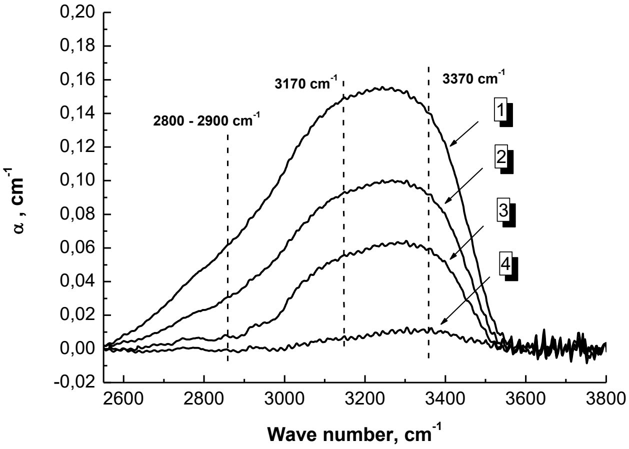

Fig. 2. Structural dependence of absorption band of OH-groups in 0.78 TeO_2 – 0.22 WO_3 glass upon concentration of water vapors over the melt.

Conditions: melt temperature is 800 ºC; melt duration is 2 hours. Water concentration over the melt (ppm vol):

1 – 50; **2** – 18; **3** – 8; **4** – 1

The shape of absorption bands is complicated since it is composed at least of three peaks of gauss form which suggests several possible variants of introduction of OH-groups into glass matrix. Decomposition of absorption band using Gaussians gives the peak positions at 2900, 3170 and 3370 cm^{-1}. The decreasing of OH-groups content in glasses changes the shape of absorption band, i.e., the band at ~2900 cm^{-1} disappears and there is an increase in the ratio between 3350-3370 cm^{-1} and 3150-3170 cm^{-1} band. In accordance with the results of [17] in absorption spectra of 0.8 TeO_2 – 0.1 Na_2O – 0.1 ZnO glass the absorption band ≈3300 cm^{-1} is connected with vibrational modes of free bond Te-OH, the bands ≈3060 cm^{-1} and ≈2290 cm^{-1} are connected with Te-OH groups forming additional weak and strong hydrogen bonds, respectively. Despite the different glass composition in our work and in [17], the first two bands have approximately the same position, and the band at 3350-3370 cm^{-1}, dominating in our driest glasses, is probably connected with vibrations of free Te-OH bond.

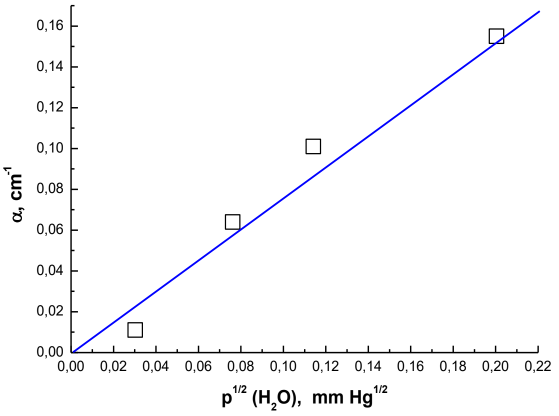

Fig. 3. Dependence of absorption coefficient in the band peak of OH-groups in 0.78 TeO_2 – 0.22 WO_3 glass upon p ½ of water above the melt.

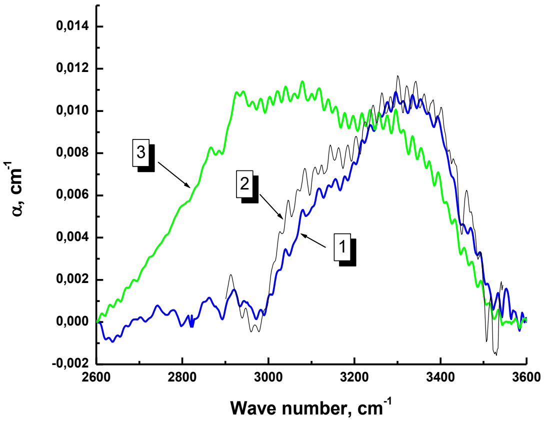

Fig. 4. Absorption bands of OH-groups in tellurite glasses of different composition: (1) TWO - 0.78 TeO_2 – 0.22 WO_3 (2) TWLO - 0.74 TeO_2 – 0.22 WO_3 – 0.04 La_2O_3 (3) TZO - 0.8 TeO_2 – 0.2 ZnO Concentration of water over the melt 1÷2·ppm vol.; melt temperature 800⁰C, melting time 2 hours.

The shape of absorption bands of hydroxyl groups in zinc- and tungsten-tellurite glasses are compared in Fig. 4. Addition of up to 8 mol.% La_2O_3 to tungsten-tellurite glasses did not lead to substantial change in the shape of absorption band of OH-groups. In contrast to $TeO_2 – WO_3$ glasses, the glasses of TeO_2 – ZnO system are characterized by a broader absorption band since ~2900 cm^{-1} band maintained even at low concentrations of OH-groups. The band at ≈2290 cm^{-1}, observed in [17], is characteristic of the glasses with high content of hydroxyl group and it was not observed in our glasses.

The content of hydroxyl groups in 0.78 TeO_2 – 0.22 WO_3 glass is linearly dependent upon square root of water pressure over the melt which proves the reaction of heterogeneous interaction between water vapors and the melt of tellurite glass [18]:

$$H_2O_{\text{vapor}} + \text{Te-O-Te}_{\text{melt}} \leftrightarrow 2\ \text{Te-OH}_{\text{melt}}$$

The synthesis of glasses in the flow of oxygen, purified from hydrocarbons and water vapors, made it possible to produce glasses of different composition with low content of hydroxyl groups. Fig. 5 presents the values of intensity of OH-group band in dependence upon the content of water in oxygen at the reactor output and the time-temperature parameters of the melting process for zinc-tellurite, tungsten-tellurite, and tungsten-tellurite with addition of lanthanum oxide glasses.

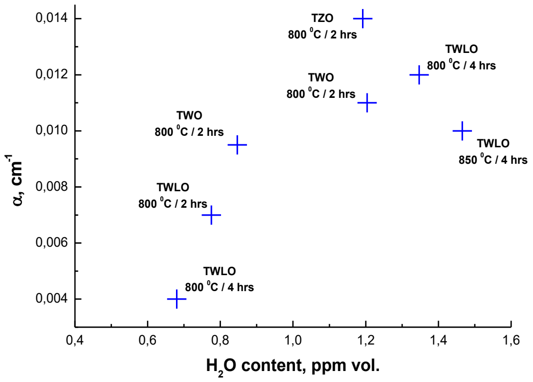

Fig. 5. Dependence of absorption coefficient in the band maximum of OH-groups in tellurite glasses upon pressure of water vapors over the melt and production conditions (temperature and melting time) TWO - 0.78 TeO_2 – 0.22 WO_3 TWLO - (0.70÷0.76) TeO_2 – 0.22 WO_3 – (0.02÷0.08) La_2O_3 TZO - 0.8 TeO_2 – 0.2 ZnO.

The content of OH-groups in glasses is mainly determined by background content of water in oxygen environment during synthesis. The magnitude for the maximum of OH-group absorption band for zinc-tellurite glasses was slightly higher as compared with that for tungsten-tellurite glasses under the same production conditions. Addition of 2-8 mol.% lanthanum oxide actually does not affect the magnitude of absorption coefficient in OH-groups. Increase in duration and temperature of synthesis leads to some decrease in the content of hydroxyl groups in glasses. According to [10, 11], where the extinction coefficients were experimentally determined for the water impurity in tellurite glasses of different composition, the concentration of OH-groups in the produced samples was at the level of several ppm mol.

At these low concentrations a noticeable contribution to the measured absorption values could be made by molecules of water dissociated on sample surfaces and diffused into near-surface layer during their annealing or polishing. As it is seen from Fig. 6, annealing of samples with the content of OH-groups at the level of 3 ppm mol. in ambient air leads to increase in concentration of OH-groups by 30-40 %.

With the goal to reduce this effect, the samples were annealed at $T=T_g + 5\ ^0C$ in the flow of "dry" oxygen (the dew point is better than $-70\ ^0C$), and optical losses for the same sample were measured at different optical path length. It permits to separate the bulk and surface constituents of optical absorption.

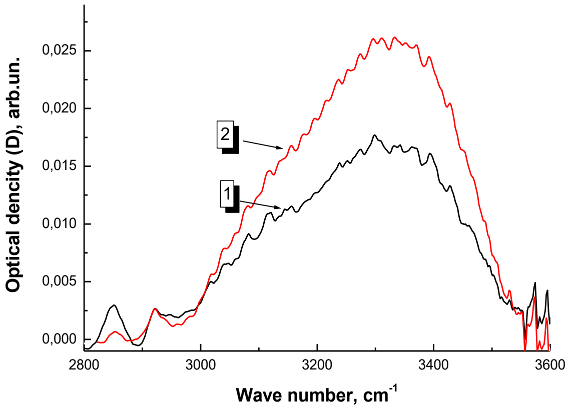

Fig. 6. Spectrum of absorption band of OH-groups in tellurite glass before (1) and after (2) annealing in laboratory air.

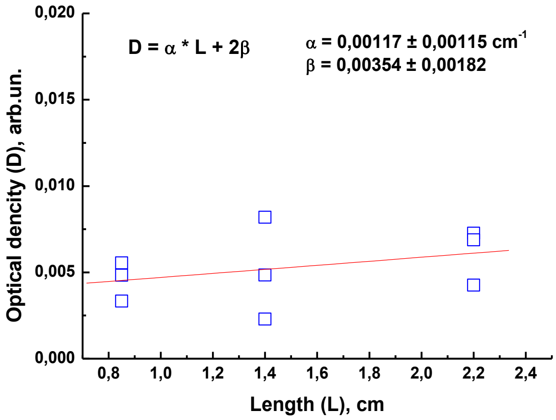

Fig. 7. Dependence of optical density upon the sample length for 0.78 TeO_2 – 0.22 WO_3 glass sample with the minimum content of OH-groups.

The dependence of optical density ($D=\ln(I_0/I)$, relative units) of our "driest" of 0.78 TeO_2 – 0.22 WO_3 glass upon the optical path length is given in Fig. 7. The optical density of sample can be represented as:

$$D = \alpha \cdot L + 2\beta,$$

where L is the sample thickness (cm), α is the coefficient of bulk optical absorbance (cm^{-1}), β is the dimensionless coefficient accounting for the absorption due to surface. It is seen from the experimental dependence that the contributions of surface and volume of this sample to optical losses are comparable. The value for coefficient of volume absorption α of the sample at 3000-3300 cm^{-1} is at the limit of detection for IR Fourier spectroscopy (0.001–0.002 cm^{-1}), which is the best of the data published for tellurite glasses. According to literature magnitude for extinction coefficient of OH-groups in tungsten-tellurite glass [10], this value corresponds to the content of hydroxyl-ions at the level of ≤ 0.5 ppm mol. The value of bulk absorption coefficient at 1.06 μm measured by method of laser calorimetry in one of the glass samples with 0.78 TeO_2 – 0.22 ZnO composition was equal to 150 dB/km.

4. Conclusion

The paper considers the production of glasses with TeO_2 – ZnO и TeO_2 – WO_3 composition with the total content of transition metal impurities not more than 1 ppm wt. using high-purity initial components. A typical content of platinum impurity in zinc-tellurite glasses is 80 ±30 ppm, and in tungsten-tellurite glasses it is 10 ±3 ppm. It is shown that the content of OH-groups in glasses is proportional to square root of water vapor pressure over the melt and depends upon time and temperature of the process. The coefficient of bulk optical absorption in the best samples is not more than 0.002 cm^{-1} in the absorption maximum of hydroxyl group band ($\lambda = 3.1 - 3.2$ μm).

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*Corresponding author: churbanov@ihps.nnov.ru