

DOI: 10.18572/2619-0141-2018-2-3-53-58

Production of TeO_2 - WO_3 glasses through the batch precipitated from aqueous solutions

A.A. Sibirkin, S.A. Gavrin, M.F. Churbanov,

National Research Lobachevsky State University of Nizhny Novgorod, Gagarin Prospekt 23/2, 603950 Nizhny Novgorod, Russia

G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, Tropinin St 49, 603951 Nizhny Novgorod, Russia

A.I. Suchkov,

G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, Tropinin St 49, 603951 Nizhny Novgorod, Russia

E-mail: asibirkin@rambler.ru (A.A. Sibirkin)

The possibility of obtaining tellurite-tungstate glasses from precipitates obtained by the action of ammonia on solutions of tellurium (IV) and tungsten (VI) compounds is shown. From the mixture precipitated from hydrochloric acid solutions of tellurium (IV) and tungsten (VI) compounds, samples of tellurite-tungstate glasses containing 9, 15, 21, and 27 % mol. WO_3 are obtained from the batch precipitated from hydrochloric acid solutions of tellurium (IV) and tungsten (VI) compounds. The products of chemical transformations occurring when the batch is heated are identified, and the optimal temperature-time regimes of its homogenizing melting are found. The optical properties of the obtained glasses are characterized.

Keywords: glass, tellurium (IV), tungsten (VI), optical properties

1. Introduction

Tellurite-tungstate glasses have a wide transparency area [1, 2], resistance to the environment, resistance to crystallization [2] and significant non-linearity of optical properties [1, 2, 3], which makes them promising optical materials, including fiber optics. Traditionally, such glasses are obtained by melting a mixture of tellurium dioxide and tungsten trioxide, taken in a given ratio, and then cooling the resulting glass-forming melt. The suitability of these glasses for practical applications is determined by their transparency and homogeneity. The achievement of the necessary homogeneity of melts and glasses is ensured by the high temperature and duration of the homogenizing melting of the batch. In this case, it is possible to change the composition of the melt due to the evaporation of individual components [4, 5] and its contamination by the crucible material. In this regard, the search for new methods for the synthesis of tellurite-tungstate glasses, suggesting a reduction in the time of homogenizing melting, a decrease in its temperature and an expansion of the range of crucible materials used, is urgent.

In [6], a method for producing glasses of a similar system containing oxides of tellurium (IV) and molybdenum (VI) was proposed. This method involves obtaining precipitates of telluric and molybdic acids by the action of ammonia on hydrochloric acid solutions of tellurium dioxide and ammonium heptamolybdate. According to [14], the parti-

cle size of tellurium (IV) and molybdenum (VI) hydroxides ranged from several nanometers to several tens of nanometers, with the most probable particle size being in the range of 8–10 nm. Such a high dispersion and the associated uniform distribution of particles by volume of sediment associated with it is unattainable with the fine grinding of crystalline individual binary oxides of tellurium and molybdenum. This determines the differences of the precipitated mixture from the traditional in behavior during heating and melting. Thus, the nano-dispersed character of the batch contributed to the synthesis of complex oxide Te_2MoO_7 , which with further heating melted with an excess of oxides of tellurium or molybdenum. Homogenizing melting of the precipitated mixture is carried out at a temperature of 600 - 700°C, while this process for the mixture of crushed oxides is performed at 700 - 900°C.

The purpose of this work is to study the possibility of obtaining transparent tellurite-tungstate glasses from a precipitated batch. The study involves the exploring of regularities of joint deposition of tellurium and tungsten compounds, identification of the nature of the crystalline phases accompanying the transformation of these precipitates into a glass-forming melt, the characterisation of optical properties of the resulting glasses.

2. Experiment

To prepare the precipitated batch, the following reagents were used: pure-grade tellurium diox-

ide TeO_2 (RF Purity Standard TU 6-09-1401-76), pure-grade sodium tungstate $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (RF State Standard GOST 18289-78 reagent-grade hydrochloric acid (RF State Standard GOST 3118-77), analytical-grade aqueous ammonia (RF State Standard GOST 3760-79), distilled water (RF State Standard GOST 6709-72).

To obtain precipitates of tellurium (IV) and tungsten (VI) hydroxides, we prepared solutions for the exact dosing of the components by titration. Tellurium dioxide was dissolved in 9M hydrochloric acid, sodium tungstate dihydrate was dissolved in distilled water. Each of these solutions contained 1.00 mol / l tellurium (IV) or tungsten (VI). The volumes of the initial solutions were selected with the aim to obtain of 14 g of glass of a given composition, provided that the components of the mixture are completely precipitated from the solution. The specified volumes of the Na_2WO_4 solution were diluted with a double volume of distilled water and passed through an ion exchange column filled with the strongly acid cation exchanger CU-2 in the H^+ form. To this freshly prepared solution of tungstic acid immediately, without waiting for its coagulation and sedimentation, the appropriate volume of hydrochloric acid solution of TeO_2 was added in small portions with continuous stirring. Further, ammonia solution was added to these mixtures in small portions until $\text{pH} = 5$, ensuring proportional precipitation of the batch components [7]. The pH value was recorded using pH-meter ANION-4100.

The composition of the obtained precipitates was determined by X-ray fluorescence analysis using reference samples prepared by dissolv-

ing precise weights of tellurium dioxide and sodium tungstate dihydrate in sodium hydroxide solution. The content of the components was determined by comparing the intensities of the $K\alpha$ lines of tellurium and tungsten on an ARL OPTIM'X X-ray fluorescence spectrometer with wavelength dispersion. The relative error of determination was 1-5%.

The precipitates obtained were washed with several portions of distilled water, followed by separation by decantation, dried at room temperature and dispersed in a mortar, and then placed in porcelain crucibles. The crucibles were heated in a muffle furnace for several hours at temperatures of 250 - 550°C. The batch was melted at temperatures of 650-800°C, depending on its composition (Table 1), for 10 minutes. After that, the glass-forming melt was poured into a steel form, preheated in a muffle furnace to 300°C, and the glass was annealed in the off-furnace mode.

To compare the properties with glasses of the same composition, obtained from binary oxides, the latter were also prepared from exact weights of binary oxides, which were ground in a mortar and placed in a porcelain crucible. The charge was melted at temperatures of 800-900°C, depending on the composition (Table 1), for 10 minutes. Molding and annealing were carried out in the same way as for glasses from a precipitated mixture.

The evolution of solid phases during heating was monitored by recording powder diffraction patterns on a Shimadzu XRD-6000 X-ray diffractometer in the 2θ angle range from 10 to 60 degrees with a step of 0.02 degrees. The studied sam-

Table 1. Temperatures of homogenizing melting of the initial batch

Composition	Liquidus temperature (°C) [13]	Melting temperature (°C) for batch obtained from	
		acids and salts	binary oxides
$(\text{TeO}_2)_{0.91}(\text{WO}_3)_{0.09}$	697	750	850
$(\text{TeO}_2)_{0.85}(\text{WO}_3)_{0.15}$	660	750	850
$(\text{TeO}_2)_{0.79}(\text{WO}_3)_{0.21}$	625	650	800
$(\text{TeO}_2)_{0.73}(\text{WO}_3)_{0.27}$	793	800	900

Table 2. Transmission boundaries of tellurite-tungstate glasses

WO_3 content (% mol)	Binary Oxide Glasses		Precipitated Batch Glasses	
	Shortwave transmission band (μm)	Longwave transmission band (μm)	Shortwave transmission band (μm)	Longwave transmission band (μm)
9	0.452	5.25	0.444	5.37
15	0.464	5.10	0.454	5.22
21	0.470	5.16	0.458	5.14
27	0.457	5.11	0.465	5.16

ples were successively maintained at temperatures of 250, 350, 450, and 550°C in air for 4 hours.

The obtained glass samples were studied by optical spectroscopy in the wavelength range of 0.4–25 μm. The transmission spectra of the synthesized glasses were recorded on a Shimadzu UV-3600 spectrophotometer in the wavelength range of 400–2500 nm with a scanning step of 2 nm and a Shimadzu IR-21 Prestige IR Fourier spectrometer in the wave number range from 400 to 7800 cm⁻¹. The spectra recorded on these instruments were combined.

3. Results

Fig. 1 shows the diffractograms of the batch of (TeO₂)_{2/0.79}(WO₃)_{0.21} composition, kept at different temperatures.

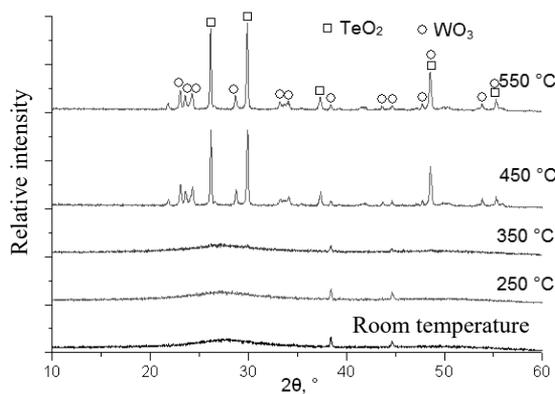


Fig. 1. Identification of crystalline phases in the batch for obtaining a glass with (TeO₂)_{2/0.79}(WO₃)_{0.21} composition

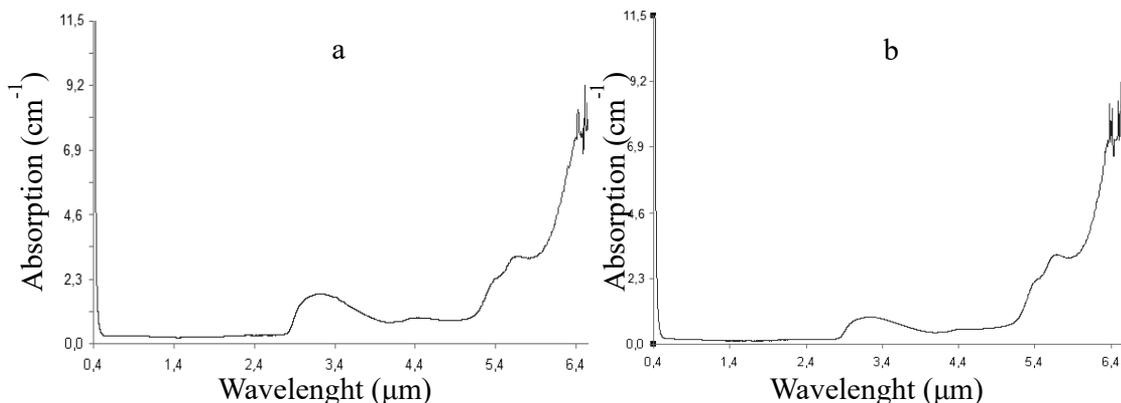


Fig. 2. Absorption spectrum of glass with (TeO₂)_{2/0.91}(WO₃)_{0.09} composition: a – from precipitated batch, b – from binary oxides.

Table 3. The band gap and the energy of the Urbach for tellurite-tungstate glasses obtained from the precipitated batch

WO ₃ content (% mol)	E _g (eV)	ΔE (eV)
9	2.66±0.11	0.122±0.001
15	2.58±0.15	0.113±0.001
21	2.59±0.12	0.100±0.001
27	2.54±0.09	0.096±0.003

A typical absorption spectrum of glasses is shown in Fig. 2. Table 3 summarizes the values of the shortwave and longwave transmission boundaries of the samples. The wavelength at which the transmission of a sample with 1 cm thick was 10% (absorption level 2.3 cm⁻¹) in the region of the short-wave or long-wavelength edges of the transmission was taken as the transmission boundary. The transparency region of the obtained glass samples is in the wavelength range from 0.44 μm to 5.4 μm and slightly decreases with increasing tungsten content. The nature of the batch does not significantly affect the position of the transmission boundaries.

4. Discussion

The co-precipitation of telluric and tungstic acids is based on their low solubility in water in a weakly acidic medium. Thus, according to [8], telluric acid in the form of TeO₂·xH₂O hydrate precipitates in the pH range from 0.7 to 8. The minimum solubility of telluric acid is observed at pH 4–5 and is 6.3 · 10⁻⁶ mol/l at pH 4.5 [7]. At pH > 8, it goes into solution to form tellurites.

Tungsten acid precipitates in a strongly acidic medium [10], but at $\text{pH} > 2$, freshly precipitated acid begins to pass into solution in the form of meta-tungstates [9, 10]. Thus, by adding ammonia to a strongly acidic solution of tellurium (IV) and tungsten (VI) compounds, co-precipitation of the desired components can be achieved.

In [7], the regularities of co-precipitation of tellurium (IV) and tungsten (VI) compounds from hydrochloric acid solutions by the action of ammonia were investigated. It was found that proportional precipitation of the components of the mixture takes place in the pH range from 2 to 7. A sufficiently large length of this interval, exceeding the co-precipitation of telluric and tungstic acids from individual solutions, indicates the occurrence of chemical interaction of these substances during the deposition. The likely product of their interaction is the ammonium salts of heteropoly compounds of tellurium (IV) and tungsten (VI). Such compounds, which are formed under similar conditions, are described, for example, in [11, 12]. The amorphous nature of the precipitation obtained during the study did not allow to understand the nature of specific representatives of such heteropoly compounds among the possible ones by X-ray phase analysis.

4.1. The evolution of crystalline phases during the heating of the precipitated batch

Samples of the precipitated batch of different compositions, both directly after drying, and kept at temperatures of 250°C, 350°C, 450°C and 550°C, were studied by X-ray phase analysis for the formation of crystalline phases in them. This allowed us to reveal the chemistry of the processes occurring in the mixture during the synthesis of glass.

It is found that in the process of heat treatment, precipitates remain amorphous, if the temperature does not exceed 350 °C. At temperatures from 450 °C and above, the mixture turns into a mixture of crystalline TeO₂ and WO₃. With increasing temperature above 620 °C, they gradually melted, without undergoing chemical changes. This temperature corresponds to the melting point of the eutectic binary system TeO₂ - WO₃, containing 21% WO₃ [13].

4.2. The influence of the temperature of homogenizing melting of the batch on the optical homogeneity of glass

To obtain all the above-mentioned glass samples, homogenizing melting of the batch was carried out for 10 minutes. Such a short melting revealed the advantages of using a precipitated mixture over the traditional batch. For each of the compositions, an attempt was made to convert the melts obtained at the lowest possible temperature into glasses. Sample preparation was considered successful if it was visually transparent, did not ex-

hibit opalescence, did not possess single (flaky) or mass crystalline inclusions. In that case, if the sample had such defects, the synthesis temperature was recognized as insufficient, and the experiment was carried out with the same sample of charge at a temperature higher than the previous by 50°C. In this way, temperature values that ensure the visual microhomogeneity of the glasses with a holding time of 10 minutes were found. Such minimum temperatures in increments of 50 °C were taken as the minimum recommended values. They are systematized in Table 1.

Found recommended melting points of the mixture of binary oxides generally correspond to the temperature of the synthesis of tellurite-tungstate glasses, known from the literature [2, 13, 17, 20, 21].

In experiments with a mixture of binary oxides, it was found that the composition $(\text{TeO}_2)_{0.79}(\text{WO}_3)_{0.21}$ has the lowest among the studied temperature of the homogenizing melting (800°C). Samples of $(\text{TeO}_2)_{0.91}(\text{WO}_3)_{0.09}$ and $(\text{TeO}_2)_{0.85}(\text{WO}_3)_{0.15}$ with a lower content of tungsten trioxide should be subjected to homogenization at 850°C. The mixture with composition $(\text{TeO}_2)_{0.73}(\text{WO}_3)_{0.27}$ with the highest among the tested samples content of refractory tungsten trioxide forms a melt that is homogenized at 900°C.

These values substantially exceed the liquidus temperatures of the corresponding compositions from the phase equilibrium diagram of the TeO₂ - WO₃ system [13]. Thus, for the composition $(\text{TeO}_2)_{0.79}(\text{WO}_3)_{0.21}$, which is close to eutectic, the recommended temperature of homogenizing melting is 800°C, while the eutectic temperature of the TeO₂ - WO₃ system is 622°C [13]. For compositions with lower than in eutectic content of WO₃, namely $(\text{TeO}_2)_{0.91}(\text{WO}_3)_{0.09}$ and $(\text{TeO}_2)_{0.85}(\text{WO}_3)_{0.15}$, the recommended temperature of homogenizing melting was 850°C. For glass $(\text{TeO}_2)_{0.73}(\text{WO}_3)_{0.27}$, close to the boundary of the glass transition region, the temperature of homogenizing melting was chosen to be 900°C. Thus, only overheating of the batch from binary oxides at 100–200°C compared with the liquidus temperature provides a complete transition into the melt of the charge components and allows one to obtain glass free from visually observed crystalline inclusions.

For homogenizing melting of the precipitated mixture, it was found sufficient to withstand the melt at a lower temperature than the melts of the binary oxide mixture. The precipitated mixture of the composition close to the eutectic, namely, $(\text{TeO}_2)_{0.79}(\text{WO}_3)_{0.21}$, was melted at 650°C. Two melts, characterized by a high content of tellurium dioxide, $(\text{TeO}_2)_{0.91}(\text{WO}_3)_{0.09}$ and $(\text{TeO}_2)_{0.85}(\text{WO}_3)_{0.15}$, were successfully homogenized at 750°C. The melt of the composition $(\text{TeO}_2)_{0.73}(\text{WO}_3)_{0.27}$, containing the greatest amount of refractory tungsten trioxide,

was cured at 800°C before curing. The listed temperatures of homogenizing melting exceed the liquidus temperatures of the corresponding compositions by 10 - 90°C. Thus, the use of the precipitated mixture makes it possible to reduce the temperature of the homogenizing melting by 100-150 °C compared to the mixture of binary oxides.

4.3. Optical properties

In the transmission spectra of all the samples obtained, two broad bands with maxima at 3.2 μm and 4.4 μm are observed, which are the absorption bands of hydroxyl groups in tellurite tungstate glasses [15, 16]. In the long-wavelength part of the transmission region of glasses, there are two partially overlapping absorption bands with maxima at 5.3 μm and 5.6 μm, which determine the position of the long-wavelength boundary of the transmission region (Table 2). It is believed that these bands represent the first overtone of asymmetric vibrations of the W = O bonds in single and twin O = WO₅ fragments of the glass mesh and with a combination of W - O - W and W = O vibrations in the adjacent O = WO₅ fragments of the glass mesh, respectively [2, 22].

For samples of glasses obtained from the deposited batch, the optical band gap E_g and the Urbach energy ΔE were calculated. The width of the optical band gap was calculated according to the Davis-Mott rule [23]:

$$\alpha h\nu = A \cdot (h\nu - E_g)^n,$$

where α is absorption, A is a constant, n is a number characterizing the mechanism of radiation absorption, and $n = 2$, corresponding to an indirect transition, was taken for most glassy tellurite systems [23], E_g is the optical width of the band gap.

The Urbach energy, which characterizes the length of the tail part of the absorption band associated with the absence of long-range order, was calculated according to the Urbach rule [1, 23]:

$$\alpha(\nu) = B \cdot \exp(h\nu/\Delta E),$$

where B is a constant, $\alpha(\nu)$ is the absorption of radiation with a frequency ν , ΔE is the Urbach energy.

The optical band gap of glasses obtained from the deposited mixture covers an interval of 2.54 - 2.66 eV. In Table 3, the standard deviation of this value, which corresponds to the limits of the confidence interval, containing ~68% of the values of the total population, is used as an error in determining the optical width of the band gap. These confidence intervals overlap each other. This means that the value found can characterize each of the studied samples, despite the difference in averages. Thus, the E_g value of tellurite tungstate glasses can be taken equal to 2.6 eV, regardless of their composition.

The values of E_g found are in good agreement with the results of measurements of the optical band gap in triple tellurite tungstate glasses. Glass-

es $(90 - x)\text{TeO}_2 - 10\text{GeO}_2 - x\text{WO}_3$ (where $7.5 \leq x \leq 30$) are characterized by E_g values in the interval 2.676 - 2.845 eV. This value decreases monotonically with increasing content of WO₃ in glasses [18]. Close values of the optical band gap of 2.47 - 2.70 eV were obtained for glasses of the $(90 - x)\text{TeO}_2 - x\text{WO}_3 - 10\text{Bi}_2\text{O}_3$ system (where $20 \leq x \leq 30$) by the authors [3].

The synthesized glasses are characterized by the Urbach energy ΔE in the range of 0.096 - 0.122 eV (Table 3). These values agree well with the results of measurements for the same binary system, for example, with values of 0.11 ± 0.14 eV [17]. The values of the Urbach energy depend on the composition of the glass, monotonously decreasing with increasing content of tungsten trioxide. A similar dependence of ΔE on the content of WO₃ is observed for germanium-containing tellurite-tungstate glasses, the Urbach energy of which is 0.178 - 0.163 eV [18].

5. Conclusion

A series of samples of tellurite-tungstate glasses with a content of WO₃ varied from 9 to 27 mol% was obtained. It has been shown that the use of the precipitated batch makes it possible to reduce the temperature and duration of homogenizing melting as compared with those in experiments on the production of TeO₂ - WO₃ glasses from binary oxides.

The products of phase transformations occurring when the precipitated batch is heated to its melting are identified. It was found that precipitated amorphous tellurium (IV) and tungsten (VI) compounds, when heated above 350°C, turn into crystalline tellurium dioxide and tungsten trioxide, which do not undergo further changes until the mixture melts.

The optical properties of the obtained glasses were characterized by optical spectroscopy. It was found that their transparency region is in the wavelength range from 0.44 μm to 5.4 μm. The obtained glass samples are characterized by an optical width band gap in the interval 2.54 - 2.66 eV. The Urbach energy of the obtained glass samples was in the range of 0.096 - 0.122 eV and decreases monotonically with an increase in the content of tungsten trioxide.

Acknowledgements

The work was performed as part of the state assignment on project No. 4.5706.2017/БЧ.

References

- [1] Raouf A.H. El-Mallawany, Tellurite Glasses Handbook: Physical Properties and Data, CRC Press, New York, 2001.
- [2] V.V. Dorofeev, A.N. Moiseev, M.F. Churbanov, T.V. Kotereva, A.V. Chilyasov, I.A. Kraev, V.G. Pimenov, L.A. Ketkova, E.M. Dianov, V.G. Plotnichenko, A.F. Kosolapov, V.V. Koltashev, Produc-

- tion and properties of high purity $\text{TeO}_2\text{-WO}_3\text{-(La}_2\text{O}_3, \text{Bi}_2\text{O}_3)$ and $\text{TeO}_2\text{-ZnO-Na}_2\text{O-B}_2\text{O}_3$ glasses, *Journal of Non-Crystalline Solids*. 357 (2011) 2366–2370.
- [3] Y. Chen, Q. Nie, T. Xu, S. Dai, X. Wang, X. Shen, A study of nonlinear optical properties in $\text{Bi}_2\text{O}_3\text{-WO}_3\text{-TeO}_2$ glasses, *Journal of Non-Crystalline Solids*. 354 (2008) 3468–3472.
- [4] J.R. Soulen, P. Sthapitanonda, J.L. Margrave, Vaporization of inorganic substances: B_2O_3 , TeO_2 and Mg_3N_2 , *Journal of Physical Chemistry*. 59(1) (1955) 132–136.
- [5] E.K. Kazenas, M.A. Bol'shikh, Evaporation of SeO_2 , TeO_2 oxides, *Metally*. 2 (1996) 9–16. [*in Russian*]
- [6] M.F. Churbanov, A.A. Sibirkin, O.A. Zamyatin, The method of obtaining highly pure tellurite-molybdate glasses, patent of the Russian Federation 2484026. Published in Bulletin 16 10.06.2013.
- [7] A.A. Sibirkin, S.A. Gavrin, A.I. Suchkov, O.A. Zamyatin, M.F. Churbanov, Coprecipitation of Tellurium(IV) and Tungsten(VI) Hydroxides from Aqueous Solutions, *Inorganic Materials*. 51(6) (2015) 627–630.
- [8] I.I. Nazarenko, A.N. Ermakov, Analytical chemistry of selenium and tellurium, Nauka, Moscow, 1971. [*in Russian*]
- [9] M. V. Mokhosoev, N. A. Shevtsova, The state of molybdenum and tungsten ions in aqueous solutions, Buryat book publishing house, Ulan-Ude, 1977. [*in Russian*]
- [10] A. N. Zelikman, L. S. Nikitina. Tungsten, *Metallurgiya*, Moscow, 1978. [*in Russian*]
- [11] C. Ritche, K.G. Alley, C. Boskovic, Lanthanary Tungstotellurates(IV): $[\text{Te}_2\text{W}_{17}\text{O}_{61}]^{12-}$, $[\text{Te}_2\text{W}_{16}\text{O}_{58}(\text{OH})_2]^{14-}$ and $[\text{Te}_2\text{W}_{18}\text{O}_{62}(\text{OH})_2]^{10-}$, *Dalton Trans.* 39 (2010) 8872–8874.
- [12] A.H. Ismail, N.H. Nsouly, M.H. Dickman, J. Knez, U. Kortz, The 20-Tungsto-4-Tellurate(IV) $[\text{H}_2\text{Te}_4\text{W}_{20}\text{O}_{80}]^{22-}$ and the 15-Tungstotellurate(IV) $[\text{NaTeW}_{15}\text{O}_{54}]^{13-}$, *Journal of Cluster Science*. 20 (2009) 453–465.
- [13] S. Blanchandin, P. Marchet, P. Thomas, J.C. Champarnaud-Mesjard, B. Frit, A. Chagraoui, New Investigations within the $\text{TeO}_2\text{-WO}_3$ System: Phase Equilibrium Diagram and Glass Crystallization, *Journal of Materials Science*. 34 (1999) 4285–4292.
- [14] M.F. Churbanov, A.A. Sibirkin, O.A. Zamyatin, I.G. Goreva, A.N. Moiseev, A.I. Suchkov, T.A. Gracheva, Preparation and optical properties of tellurite-molybdate glasses, The International Symposium on non-oxide glasses and new optical glasses, July 1st-5th 2012, Saint-Malo, France.
- [15] B.V. Tatarintsev, A.K. Yahkind, The effect of water on the infrared transmission of highly refractive tellurite glasses and the method of its quantitative determination, *Optiko-mekhanicheskaya promushlennost'*. 10 (1972) 72–73. [*in Russian*]
- [16] B.V. Tatarintsev, A.K. Yahkind, The mechanism of dehydration of tellurite glass-forming melts, *Optiko-mekhanicheskaya promushlennost'*. 4 (1975) 34–37. [*in Russian*]
- [17] S.K. Al-Ani, S.A. Hogarth, R.A. L-Malawany, A study of optical absorption in tellurite and tungsten-tellurite glasses, *Journal of Materials Science*. 20 (1985) 661–667.
- [18] G. Upender, Ch. Sameera-Devi, V. Chandramouli, Role of WO_3 on DC Conductivity and Some Optical Properties of TeO_2 Based Glasses, *Materials Research Bulletin*. 47 (2012) 3764–3769.
- [19] Y. Gandhi, K.S.V. Sudhakar, M. Nagarjuna, N. Veeraiah, Influence of WO_3 on some physical properties of $\text{MO-Sb}_2\text{O}_3\text{-B}_2\text{O}_3$ ($\text{M} = \text{Ca, Pb}$ and Zn) glass system, *Journal of Alloys and Compounds*. 485 (2009) 876–886.
- [20] K. Tanaka, A. Narazaki, K. Hirao, Large optical second-order nonlinearity of poled $\text{WO}_3\text{-TeO}_2$ glass, *Optics Letters*. 25(4) (2000) 251–253.
- [21] P. Charton, L. Gengembre, P. Armand, $\text{TeO}_2\text{-WO}_3$ Glasses: Infrared, XPS and XANES Structural Characterizations, *Journal of Solid State Chemistry*. 168 (2002) 175–183.
- [22] V.V. Dorofeev, A.N. Moiseev, M.F. Churbanov, G.E. Snopatin, A.V. Chilyasov, I.A. Kraev, A.S. Lobanov, T.V. Kotereva, L.A. Ketkova, A.A. Pushkin, V.V. Gerasimenko, V.G. Plotnichenko, A.F. Kosolapov, E.M. Dianov, High-purity $\text{TeO}_2\text{-WO}_3\text{-(La}_2\text{O}_3, \text{Bi}_2\text{O}_3)$ glasses for fiber-optics, *Optical Materials*. 33 (2011) 1911–1915.
- [23] M. Elahi, D. Souri, Study of optical absorption and optical band gap determination of thin amorphous $\text{TeO}_2\text{-V}_2\text{O}_5\text{-MoO}_3$ blown films, *Indian Journal of Pure & Applied Physics*. 44 (2006) 468–472.