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# PRODUCTION OF $TeO_2$-ZnO GLASSES BY CHEMICAL VAPOR DEPOSITION FROM ORGANO-METALLIC COMPOUNDS

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A mechanically durable $TeO_2$ – ZnO (15-30 mol.% ZnO) soot is produced by CVD method from the gas phase with the use of organo-metallic compounds. The phase composition and degree of crystallization of the soot depend on the deposition substrate temperature. At deposition temperatures lower than the crystallization temperature an amorphous soot is produced with the Raman spectra being identical to the spectra of glass produced by melting oxides. The amorphous soot melts at temperatures below 400 $^0$C. At deposition temperatures exceeding 420 $^0$C the crystalline phases of $\alpha$-$TeO_2$ and $Zn_2Te_3O_8$ are determined by the methods of X-ray diffraction and Raman spectroscopy. The crystallization grows up to 90% at deposition temperatures of 620-650°C. This soot melts at 620-650°C with glass formation. The water content in glass produced by annealing of the melt in air is at the level of 100 ppm in accordance with the IR spectroscopy results. Treatment and melting of the soot in the flow of dry oxygen lowers the content of OH-groups down to 5-6 ppm.

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## 1. Introduction

Tellurite glasses are of great interest due to a broad transmission band (0.4-6 mkm), large refractive index value, and high chemical stability. A broad band of Raman amplification and a high solubility limit of rare-earth elements make them a promising material for active elements of optical fiber communication lines (OFCL) [1,2].

$TeO_2$-ZnO system was investigated in a number of studies [3-5]. This system is characterized by a wide range of glass formation (9-40 mol. % ZnO) and high stability. Investigations devoted to tellurite glasses deal usually with the method of melting the mixture of oxides in inert crucible (made of platinum or gold). Purity of glasses is determined by the purity of initial oxides. Besides, it is limited by a high temperature of oxide melting (800-1000°C), when the glass is contaminated with the crucible material. The use of volatile compounds of tellurium and zinc makes it possible to produce the initial furnace charge of a higher purity. Melting of highly dispersive homogeneous material produced from the gas phase can also be carried out at a lower temperature (650-750 °C). The data on the production of tellurite glasses from the gas phase are not available in literature.

Our paper presents the results of investigation of the properties of $TeO_2$-ZnO glasses produced from the gas phase.

## 2. Experimental

The alkyl organo-metallic compounds (OMC), i.e. dimethyltellurium ($Te(CH_3)_2$) ($T_{boil.}$ = 93 °C), diethyltellurium ($Te(C_2H_5)_2$) ($T_{boil.}$=137 °C), dimethylzinc ($Zn(CH_3)_2$) ($T_{boil.}$=44 °C) and diethylzinc ($Zn(C_2H_5)_2$) ($T_{boil.}$=118 °C) were selected as the initial volatile compounds of tellurium and zinc. These compounds were selected both due to high values of saturated vapor

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pressure and high reactivity of OMC with respect to oxygen and water. They can be easily produced in a high-purity state. The content of metal impurities in these compounds in our experiments did not exceed $10^{-5}$ mass %.

Deposition was carried out on the apparatus shown in Fig. 1. In the flow of gas-carrier, as well as oxygen and hydrogen, the initial compounds were supplied to the burner with external mixing. Argon was used as a carrier gas for organometallic compounds, interacting in oxyhydrogen burner with the flame components and between themselves. This led to the formation of a condensed phase. The flame temperature was determined by the ratio between hydrogen, oxygen, and argon and fell in the 1000-1400 $^{o}$C range. The solid soot was deposited on the side surface of the rotary moving rod (the holder) made from a silica glass or other material. Thermodynamic analysis of heterogeneous system $TeAlk_2+ZnAlk_2+O_2+H_2 \rightarrow products$ (with the oxygen abundance $O_2/H_2=2\text{-}3$) indicated an actually complete transformation of the organometallic compounds into oxide mixture at 300-800 $^{o}$C. The deposition surface temperature was controlled by IMPAC IN 5 Plus pyrometer. The holder side surface temperature was varied within 300-700 $^{o}$C by changing the distance from the burner and the hydrogen consumption (with the 2-3-fold oxygen excess).

The soot composition was set by the flow ratio of organometallic compounds. The glass composition was determined by the Raman spectroscopy after melting the residue in oxygen environment in platinum crucible at 730 $^{0}$C for 30 minutes with a subsequent quick cooling at a rate of ~10 K/s (standard melting-quenching technique).

Raman spectra were measured on Tripple Raman spectrograph T-64000 (Jobin Yvon) with the use of macro attachment at the angle of $90^{0}$.

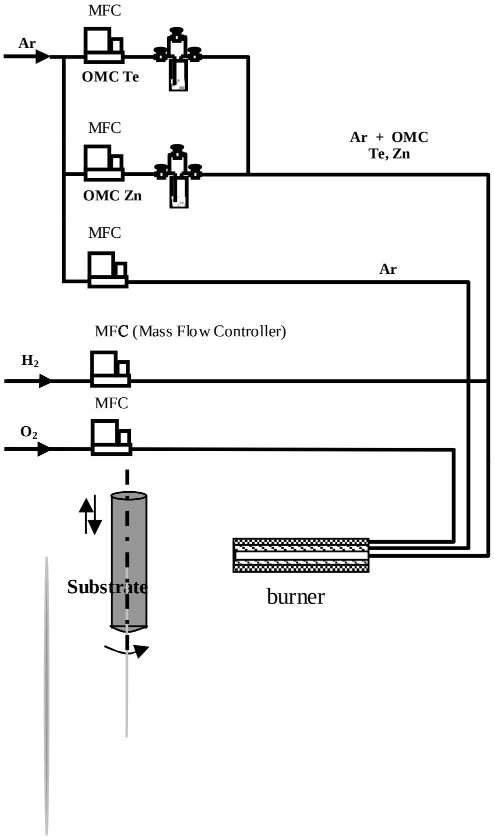

Fig. 1. Schematic diagram of apparatus for chemical deposition of $TeO_2$-ZnO from the gas phase OMC.

IR transmission spectra were measured on Fourier spectrometer Bruker IFS-113v.

The share and composition of the crystalline phase in $TeO_2$ – ZnO residue were determined by the X-ray diffraction (XRD) method on DRON-3M instrument.

## 3. Results and discussion

$TeO_2$ – ZnO powder soot with different ZnO content (15-30 mol. %) was produced. It appeared to be a mechanically tough white porous material of various densities depending on the deposition conditions, and consisted of particles with the average size of 0.5-1.0 mkm. The deposition rate for the $Te(CH_3)_2$ - $Zn(CH_3)_2$ pair was by several times higher (~10 g/hour) than that for the $Te(C_2H_5)_2$ - $Zn(C_2H_5)_2$ (~1.5-2 g/hour) pair, that could be explained by a higher volatility of methyl compounds. The total content of metal impurities in the residue was less than $10^{-4}$ mass %.

Fig. 2 shows the Raman spectra of glasses produced from the residue of $TeO_2$ – ZnO of different composition. The spectra are similar to the spectra of glasses of the same composition given in literature [5].

Fig. 3 shows the Raman spectra of $TeO_2$ – ZnO soots (~20 mole % ZnO) obtained at different side surface temperatures in a silica rod. For a comparison the Raman scattering of crystalline $\alpha$-$TeO_2$ is given below [6].

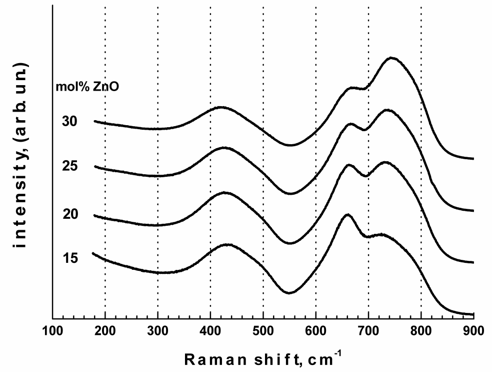

Fig. 2. Raman scattering spectra of $TeO_2$-ZnO glasses of different composition produced by CVD method.

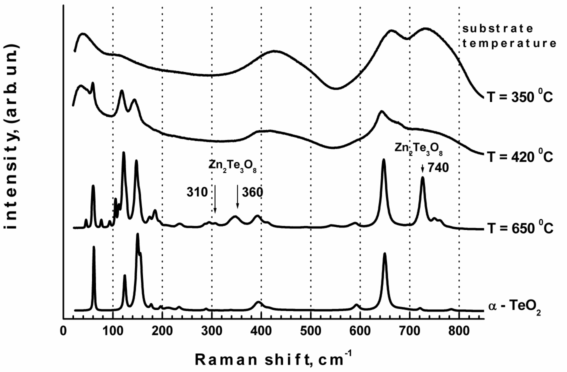

Fig. 3. Raman scattering spectra of $TeO_2$-ZnO (20 mol. % ZnO) produced by CVD method at different substrate temperatures.

The phase composition of the soot is greatly influenced by the substrate temperature. At deposition temperatures less than the crystallization temperature in glasses of the given composition (< 350 $^oC$) the Raman spectra of the soots is similar to the spectrum of glasses produced by melting oxides. With the holder temperature increasing up to 400-420 $^0C$ several broadened lines are observed in the Raman spectra concerned with $\alpha$-$TeO_2$. All that is in good agreement with the results of [7], where it is shown that the crystallization of $TeO_2$ – ZnO glass (20 mol. % ZnO) starts at 428 $^oC$ with the appearance of $\alpha$-$TeO_2$ phase. At deposition temperatures of 600-650 $^oC$ a number of sharp peaks are observed which can be related to different crystalline phases. According to [3], the lines with the peaks at 640, 600 and 400 $cm^{-1}$ are related to $\alpha$-$TeO_2$ phase. These lines may also be caused by quite probable $ZnTeO_3$ and $Zn_2Te_3O_8$ phases. The lines at 740, 360 and 310 $cm^{-1}$ observed in the spectrum are due to $Zn_2Te_3O_8$. Low-intensity non-identified peaks (550, 760 $cm^{-1}$) are present in the spectrum as well.

Investigation of the XRD spectra of $TeO_2$ – ZnO residue indicates the presence of amorphous and crystalline phases. The crystallinity of soots is determined by their production conditions. A characteristic spectrum is shown in Fig. 4. Spectra were measured in 10-45$^0$ angle range. The degree of sample crystallization was determined by the ratio of the area under the curve, corresponding to crystalline phase, to the sum of areas under the curves of crystalline and amorphous phases. A quantitative determination of crystallinity was carried out by calibration dependence registered for specially produced reference samples.

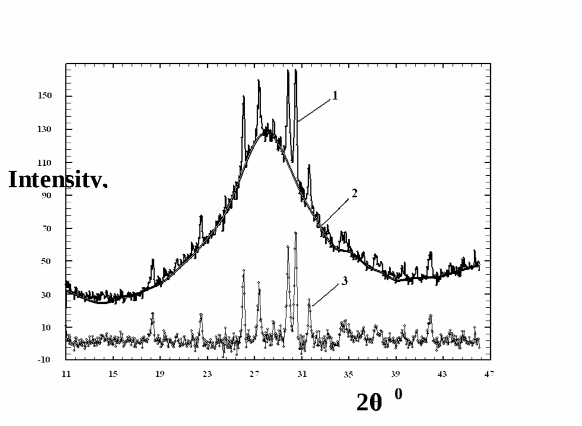

Fig. 4. X-ray diffraction spectra of $TeO_2$-ZnO soot (1) comprising the amorphous (2) and crystalline (3) constituents.

At deposition temperatures below 350 $^0$C the crystalline phase content was less than the absolute sensitivity of the given method (~2%). With the holder temperature increasing the share of a crystalline phase in the soot increases attaining 50-90 % at deposition temperatures of 500–650 $^0$C. According to the XRD data crystalline phases of $\alpha$-$TeO_2$ and $Zn_2Te_3O_8$ are present in the material.

The presence of $ZnTeO_3$ was observed in [8] at crystallization of $TeO_2$ – ZnO glasses with the content of 10-30 mol. % ZnO. It is shown that this compound can exist in a rather narrow temperature range (410-470 $^0$C for glasses with 20 mol. % ZnO). At higher temperatures only $Zn_2Te_3O_8$ is present. We did not find any noticeable amount of $ZnTeO_3$ in the residue that we have produced from the gas phase.

The transformation temperature of white crystalline residue into a transparent glass is determined by the melting temperature of the $\alpha$-$TeO_2$ and $Zn_2Te_3O_8$ mixture, being 620-650 $^0$C in the 10-30 mol. % ZnO range in accordance with the differential thermal analysis and XRD methods [8]. It was found that the amorphous $TeO_2$ – ZnO powder deposited from the gas phase converts into a transparent state at lower temperatures 340-400 $^0$C. The formed melt is not stable; at first it darkens, and then the crystallization takes place with the appearance of $\alpha$-$TeO_2$. According to the Raman spectra, darkening is due to the tellurium formation. The residues with a substantial crystalline phase content are melted at 620-650$^o$C with the formation of a stable transparent melt. The IR absorption spectra of $TeO_2$ – ZnO glasses produced by melting the soots in air in platinum crucible have a broad band with the intensity of 2-3 cm$^{-1}$ at 3000 cm$^{-1}$. It corresponds to about 100-ppm water content in glasses. In case the porous soot is sustained for 2 hours in the flow of dried oxygen (the dew-point temperature is –80 $^o$C) and then melted, the intensity of this complex absorption band decreases by 10-16 times in the 2900-3400 cm$^{-1}$ range of the glass (Fig. 5).

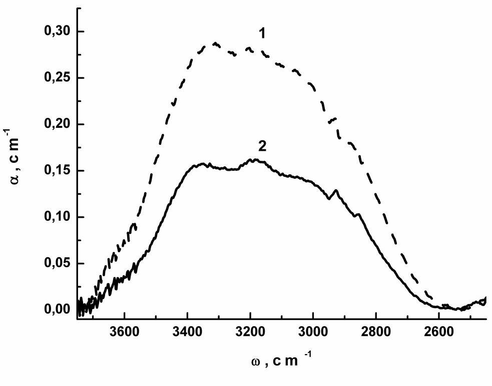

Fig. 5. IR absorption spectra of $TeO_2$-ZnO glasses after treatment and melting of the soot in dry oxygen flow: Curve 1 – at T=300 $^o$C, t=2 hours; Curve 2 – at T=600 $^o$C, t=2 hours.

## 4. Conclusion

The $TeO_2$ – ZnO (15-30 mol. % ZnO) glass system is produced by CVD method from the gas phase. The phase composition and degree of crystallization of $TeO_2$ – ZnO residues depend on the deposition surface temperature. At deposition temperatures lower than the crystallization temperature, the mechanically durable amorphous soot is produced with the transition temperatures into a transparent melt below 400 °C; however, the melt is subjected to evolution of tellurium and to crystallization. At higher deposition temperatures the share of the crystalline phase (identified earlier as the mixture of $\alpha$-$TeO_2$ and $Zn_2Te_3O_8$) is increased in the soot. The melting temperature of this soot is 620-650 °C depending on the composition. The water content in it is about 100 ppm without additional drying, being below 5-6 ppm at the soot heating and melting into glass in the dried oxygen.

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