Changes of a refractive index of tellurite glass

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Abstract—The goal of this work was to investigate the influence of rare earth ions such as Tm^{3+}, Yb^{3+} on physico-chemical properies of tellurite glass from the TeO_2-WO_3-PbO-PbF_2-Na_2O system. The thermal characteristics of tellurite glass Tm^{3+}, Yb^{3+} doped have been presented. The effect of the glass crystallization on thermal stability of the glass and crystallizing phases formed upon heat treatment were investigated by DTA/DSC/, XRD methods. The influence of ions of rare earth elements, i.e. Tm^{3+} and Yb^{3+}, onto changes of refractive index of tellurite glass were examined.

Among numerous oxide glasses, tellurite glasses of the system TeO_2-WO_3-PbO, have unique optical and magneto-optical properties, resulting from big mass and polarizability of Pb^{2+} ions. They are characterized by a high refractive index of about 2.0, as well as an absorption edge located at 6 μm [1]-[3]. High value of the refractive index of tellurite glasses allows using such materials in optical waveguides, where a self-focusing effect is observed [4, 5]. They are used in infrared optics, optical-electronics, magneto-optics, as well as in optical waveguide technology [6,7].

The following raw materials were used to prepare the batches: TeO_2, WO_3, PbO, Na_2O, PbF_2, Tm_2O_3, Yb_2O_3. The batches were based on the TeO_2-WO_3-PbO-PbF_2-Na_2O tellurite glass system, with rare earths admixtures: Tm^{3+}, Yb^{3+}. For each batch, high purity initial materials were fully mixed and melted in covered gold crucibles in an electric furnace at a temperature of 850ºC, in air atmosphere. The compositions of glasses are listed in Table 1.

Table.1. Chemical composition of glass.

Glass No.	Chemical composition in % mole						
	TeO_2	WO_3	PbO	Na_2O	PbF_2	Tm_2O_3	Yb_2O_3
P1	60	28	2	2	8	-	-
P2	60	28	7	2	3	0,08	-
P3	60	28	7	2	3	-	0,08

The crystallization ability of obtained glasses was determined on the basis of DTA/DSC measurements, conducted on a Perkin-Elmer DTA-7 system, operating in the heat flux DSC mode. The spectroscopic measurements of Ψ and Δ of the presented glasses were made using a Woollam M2000 spectroscopic ellipsometer, in a spectral range of 190-1700 nm. The samples were measured for three angles of incidence (55º,60º,65º). Ellipsometric parameters (angles Δ and ψ) were determined with accuracy of about 0,01°, according to the basal ellipsometric relation:

$$\rho = \left|\frac{r_p}{r_s}\right| e^{i\Delta} = tg(\Psi)e^{i\Delta} \qquad (1)$$

During the heat treatment, tellurite glasses from the TeO_2-WO_3-PbO-PbF_2-Na_2O system with admixtures of rare earths Tm^{3+}, Yb^{3+}, beside thermal effects characteristic for standard modification of the glassy state, expose an additional exothermal effect located near transformation temperature T_g. This effect is related with fluoride phase crystallization of the type: lead fluoride with included ions of RE elements (Yb^{3+}, Tm^{3+}) (Fig.1).

The presence of the crystalline phase within the range of the effect occurrence was proved with X-ray phase analysis XRD (Tab.2.). Based on the analysis of the DTA/DSC curves of glasses P1, P2, P3, it was proved that the presence of a clearly visible exothermal effect within the temperature range 500°C–600°C is directly related with the PbF_2 nanocrystallization process. In the examined group of glasses P1, P2, P3, differing in their admixture type in the form of rare earths, the influence of the RE type onto glassy state transformation, as well as onto crystallization process, was observed. For glasses P2, P3 with Tm^{3+}, Yb^{3+} ion admixtures, the transformation temperature is displaced toward higher temperatures, as compared with the reference glass (1) without any admixture (Table.2). Simultaneously, the glassy state

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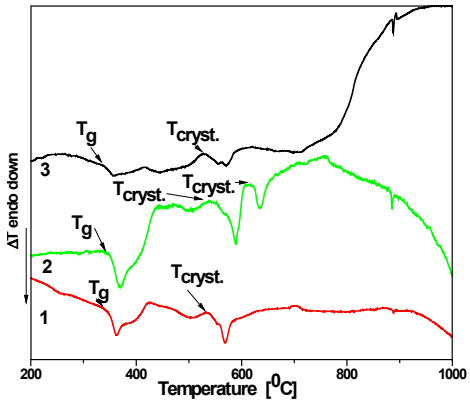

Fig.1. DTA/DSC curves of tellurite glasses.

transformation temperature rise is accompanied by smaller changes of mole heat ΔC_p, which can indicate a strength increase, as well as elasticity improvement of the glasses in question. Under the influence of the admixture, also the temperature of a maximal crystallization effect is displaced toward higher temperatures. The values of heat parameters – drop of thermal stability ΔT in glasses P1, P2 are indicative of better ceramization of glasses – up to fluoride phase crystallization in the form of PbF_2 nano-crystallites (Table.2).

Table 2. Characteristic temperatures of tellurite glasses

Sample No	T_g [°C]	ΔC_p [J·g^{-1}·°C^{-1}]	$T_{max\ cryst.}$ [°C]	ΔH [J·g^{-1}]	$\Delta T = T_{cryst.} - T_g$ [°C]	Type of crystallization phase
P1	340	0,197	528	21,56	188	TeO_2
P2	358	0,296	553 620	20,78 20,34	195 262	TeO_2 PbF_2
P3	347	0,196	527	23,54	180	PbF_2

The spectral dependence of ellipsometric angles of the P1, P2 and P3 glass samples has been shown in Fig. 2.Additionally, generated values of Ψ and Δ obtained from the Cauchy model have been presented in Fig. 2.
The Cauchy model describes dispersion relations for *n* and *k* indices, namely:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \qquad (2)$$

$$k(\lambda) = Ke^{\beta(\frac{hc}{\lambda} - E_{bandedge})} \qquad (3)$$

where A,B,C and and β are constants. K and $E_{Bandegde}$ are the fit parameters describing the Urbach absorption tail and allow us to define the dispersion shape of an extinction coefficient [8]. The values of these fit parameters, for P1, P2 and P3 glass samples, have been presented in Table 3.

Table 3. Values of fitted parameters

Glass No	A (n dla 633 nm)	B 10^{-2}	C x 10^{-4}	K x 10^{-4}	r [nm]
P1	1.871 ± 0.119	1.946 ±0.028	2.641 ± 0.033	0.50± 0.020	9.27 ± 1.250
P2	1.824 ± 0.135	1.244 ±0.025	2.630± 0.036	0.164 ± 0.092	13.41 ± 1.90
P3	1.989 ± 0.070	1.511 ±0.023	0.348 ± 0.307	0.117 ± 0.019	16.39 ± 1.02

Figure 3 illustrates n and k dispersive relations within 190 to 1700 nm spectral range, determined for the studied samples.

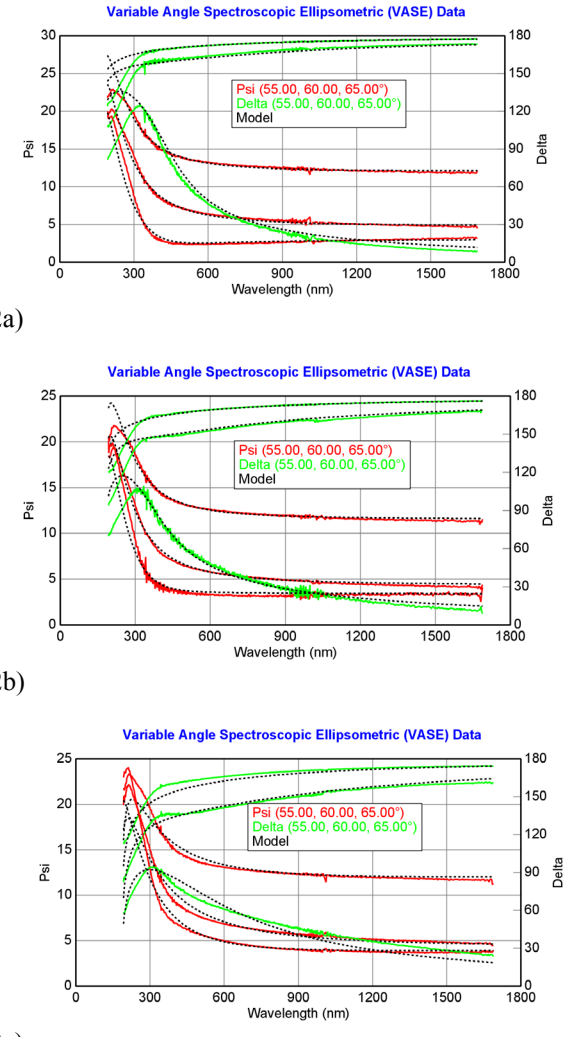

Fig. 2. Spectral dependence of ellipsometric angles Ψ and Δ measured for P1, P2, and P3 glass samples, respectively

Coefficients *n* and *k* of tellurite glasses P1, P2, P3 expressed in the wavelength function and determined on the basis of ellipsometric measurements within 190 do 1700 nm spectrum range are shown in Fig. 3.

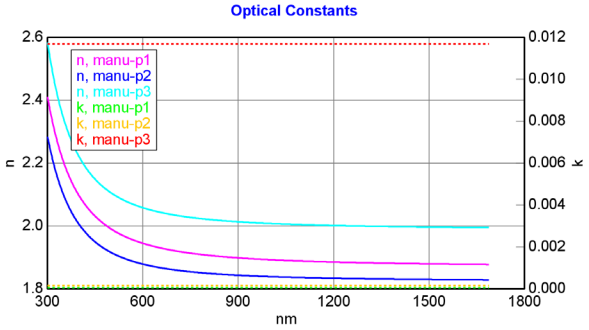

Fig. 3. Cauchy dispersion dependences of glasses P1, P2, P3 determined for *n* – and *k*.

The appearance of surface roughness, which can be described using the Bruggeman effective medium approximation (EMA), was assumed for the investigated samples [9]. This approximation uses 50:50 mixture of the material and air, at the sample surface getting optical constants that approximate the effect of surface roughness. The obtained values of σ, are presented in column 6 of Table 3.

Based on the conducted thermal examinations, it has been proved that crystallization ability of tellurite glasses of the system TeO_2-WO_3-PbO-PbF_2-Na_2O with admixtures of rare earths elements strongly depends on the RE type. It has been proved that the admixture of ions Yb^{3+} and Tm^{3+} results in the appearance of an exothermal effect related with PbF_2 crystallization on DTA/DCS curves. It has been observed in the case of glass P2, with admixtures of ions Tm^{3+}, that the crystallization process is run in two phases; within the temperature range 400-600°C. Thellurium oxide TeO_2 is a crystallization phase at a temperature of 553°C, whereas the heat treatment of this glass at 620°C causes the appearance of another low-phonon energy crystallization phase of the PbF_2 type. Based on thermal examinations of the glasses in question, it has been proved that rare earths elements which are present in the structure cause the displacement of a glassy state transformation temperature towards higher levels, and lowered values of parameters of thermal stability $\Delta T=T_{cryst.}-T_g$ indicate an improvement in a glass tendency for fluoride phase crystallization.

Refraction indexes of tellurite glasses reach very high values of over 1,85 within all measured spectral range, and they are considerably higher than in the case of standard optical glasses. Ellipsometric examinations have proved that ions of rare earth elements, i.e. Tm^{3+} and Yb^{3+}, have a considerable influence on the changes of an refractive index of basal glass P1 (without RE admixture). Doping Tm^{3+} ions to a tellurium matrix of glass from the system TeO_2-WO_3-PbO-PbF_2-Na_2O results in the reduction of a refractive index by about 0.03 (glass P2). However, doping with Yb^{3+} ions (glass P3) results in its considerable rise by about 0,12 within the visible range) with respect to base glass P1. Doped tellurite glass has also bigger roughness, whereas the highest influence on roughness rise was observed in the case of glass doped with Yb^{3+} ions.

It can be concluded that admixtures of Yb^{3+} ions have the most considerable influence on the rise in tellurite glasses refractive index r. Additional optical and thermal examinations will be conducted in order to determine the optimal contents of ytterbium ions, which change *n* values in the most effective manner.

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