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Influence of active admixtures onto tellurite glass refractive index

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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 characteristic 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 spectral dependence of ellipsometric angles of the tellurite glass samples, have been studied. The influence of ions of rare earth elements, i.e. Tm^{3+} and Yb^{3+}, onto changes of refractive index of glass P1 (without RE admixture) were examined. The optical measurements were conducted on Woollam M2000 spectroscopic ellipsometer, in spectral range of 190–1700 nm.

Key words: tellurite glass, rare earth ions, refractive index.

1. Introduction

Tellurium oxide TeO_2 plays bonding role in the structure of tellurite glasses. As a pure oxide, it has not glass-forming property, however, it exposes such property in case of participation of such oxides as: SeO_2, MoO_3, WO_3 or Bi_2O_3 [1, 2]. Among numerous oxide glasses [3], 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 characterize with high refractive index of about 2.0, as well as with absorption edge located at 6 μm [4]. High value of the refractive index of tellurite glasses allows using such materials in optical waveguides, where self-focusing effect is observed [5, 6]. They are used in infrared optics, optical-electronics, magneto-optics, as well as in optical waveguide technology. Glasses having high linear refractive index also characterize with high value of non-linear refractive index, what is, in turn, necessary when the material is used in modulators or multiplexors. They are also used as potential material applied in non-linear optics, because of the light wave changes caused by interaction with electrical, or optical field [7]. Refracting index calculated on the basis of transmission spectrum within the wavelength of 500 nm – 4000 nm does not allow obtaining information, on how its value is changed in wavelength function [8]. That is why spectroscope ellipsometry [SE] is more often applied for this purpose. SE measurements can be conducted within a range from ultraviolet light to nearest infrared, and they can be used in examination of surfaces and relatively smooth and non-dissipated layers [9].

2. Experimental procedure

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 admixtires: Tm^{3+}, Yb^{3+}. For each batch, high purity initial materials were fully mixed and melted in an electric furnace at the temperature of 850°C, in air atmosphere. The samples were placed in covered gold crucibles, with platinum cover. The melts were poured out onto a steel plate forming 2 to 5 mm thick layer, and then cast into a brass mold, followed with annealing at temperature near the glass transition temperature, determined by differential scanning calorimetry (DSC), in order to relinquish the inner stress. The compositions of the glasses are listed in Table 1.

Table 1
Chemical composition of melted glasses

Sample number	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

Crystallization ability of the obtained glasses was determined on the basis of DTA/DSC measurements, conducted on the Perkin-Elmer DTA-7 system, operating in heat flux DSC mode. The samples (60 mg) were heated in platinum crucibles, at a rate $10°C\times min^{-1}$, in dry nitrogen atmosphere, up to temperature of 1000°C. All glasses revealing the effect of crystallization were selected for further thermal treatment. X-ray phase analysis (X'Pert XRD by Philips) was used for the identification of phases developed during the glasses heat treatment.

The spectroscopic measurements of angles Ψ and Δ the presented glasses were made using Woollam M2000 spectroscopic ellipsometer, in spectral range of 190–1700 nm. Ellipsometric parameters (angles Δ and ψ) were determined with accuracy of about 0.01°, according to basal ellipsometric relation:

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

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where r_p and r_s are Fourier amplitude coefficients for polarization "p" and "s".

Suitable physical model giving consideration to geometry and optical properties of the tellurite glass samples within measured spectrum range was selected. Dispersion relations dependence of glass refractive index $n(\lambda)$, extinction coefficient $k(\lambda)$ and roughness σ were determined from the best correlation between model and experimental parameters. The samples have been measured for three angles of incidence (55°, 60°, 65°). To analyze the data, all angular spectra were combined, and all data were simultaneously fitted. The data have been analyzed using Complete EASE 3.65 software. Depolarization coefficient v.s light wavelength, have been determined, as well.

3. Experimental results

3.1. Thermal stability. During 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+}, besides thermal effects characteristic for standard modification of the glassy state, expose additional exothermal effect located near transformation temperature Tg. This effect is related with fluoride phase crystallization of the type-lead fluoride (Fig. 1). According to [10] formation of the b-PbF_2 phase during thermal treatment of glass is favoured by the incorporation of RE ions in the crystalline phase, playing the role of heterogeneous nucleating agents and partially replacing the Pb^{2+}.

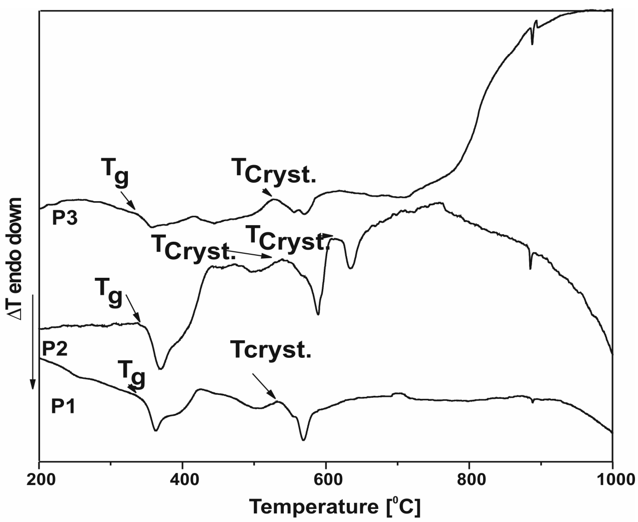

Fig. 1. DTA/DSC curves of tellurite glasses

Presence of the crystalline phase within the range of the effect occurrence was proved with X-ray phase analysis XRD (Table 2, Figs. 2, 3). Based on the analysis of the DTA/DSC curves of glasses P1, P2, P3 it was proved, that presence of well visible exothermal effect within temperature range 500–600°C is directly related with PbF_2 nanocrystallization process. In examined group of glasses P1, P2, P3, differing with admixture type in form of rare earths, influence of RE type and fluorine content onto glassy state transformation, as well as onto crystallization process, was observed. Lead fluoride addition on germanate glass suggested that when fluoride is added into germanium dioxide glass, oxygen ions can simply be replaced by fluorine ions; and that the fluorine ions then act as either non-bridging or bridging species between structural units [11]. Based on these study results, therefore, it can be inferred that in the case of fluorotellurite glass, fluorine ions depolymerize the glass structure. These effects should lead to a lowering of Tg, with with increasing concentration of PbF_2 (glass P1). For glasses P2, P3 with Tm^{3+}, Yb^{3+} ion admixtures, and lower concentration of PbF_2 transformation temperature is displaced toward higher temperatures, as compared with reference glass (P1) without admixture (Table 2). Simultaneously, glassy state transformation temperature raise is accompanied with smaller changes of mole heat ΔC_p, what can indicate for the strength increase, as well as for elasticity improvement of the glasses in question. Under influence of the admixture, and lead fluoride concentration also temperature of maximal crystallization effect is displaced toward higher temperatures. Values of the heat parameters – drop of the thermal stability ΔT in glasses P1, P2, indicate for better ceramization of the glasses – up to fluoride phase crystallization in form of PbF_2 nano-crystallites (Table 2, Fig. 3).

Table 2
Characteristic temperatures of tellurite glasses

Sample number	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	20.78	195	TeO_2
			620	20.34	262	PbF_2
P3	347	0.196	527	23.54	180	PbF_2

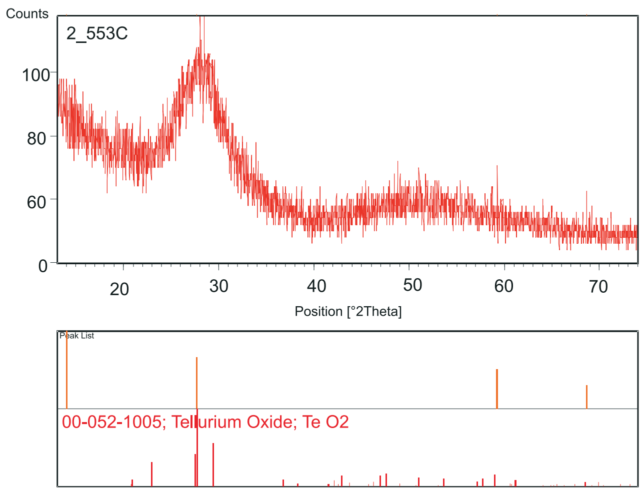

Fig. 2. Diffraction pattern of glass P2 exposed to 1 h thermal treatment in temperature of 553°C

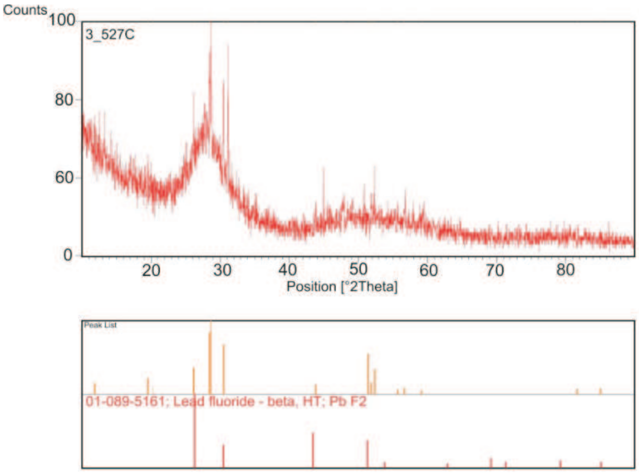

Fig. 3. Diffraction pattern of glass P3 exposed to 1 h thermal treatment in temperature of 527°C

3.2. Ellipsometric study. The spectral dependence of ellipsometric angles of the P1, P2 and P3 glass samples, have been shown in Fig. 4. Also, the generated values of Ψ and Δ obtained from the Cauchy model, have been presented in Fig. 4.

The Cauchy model describes dispersion relations for n and k indices, namely:

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

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

where A, B, C and β are constants. The k and $E_{bandedge}$ are the fit parameters describing Urbach absorption tail and allow defining the extinction coefficient dispersion shape [12]. The values of these fit parameters, for P1, P2 and P3 glass samples, have been presented in Table 3. Figure 5 illustrates n and k dispersive relations within 190 to 1700 nm spectral range, determined for the studied samples.

Coefficients n and k of tellurite glasses P1, P2, P3 expressed in wavelength function and determined on the basis of ellipsometric measurements within 190 do 1700 nm spectrum range, are shown in Fig. 5.

Appearance of the surface roughness, which can be described using the Bruggeman effective medium approximation (EMA), was assumed for the investigated samples [13]. This approximation uses 50:50 mixture of the material and air, at the sample surface getting optical constants that approximate the effect of the surface roughness. The obtained values of σ, gare presented in column 6 of Table 3.

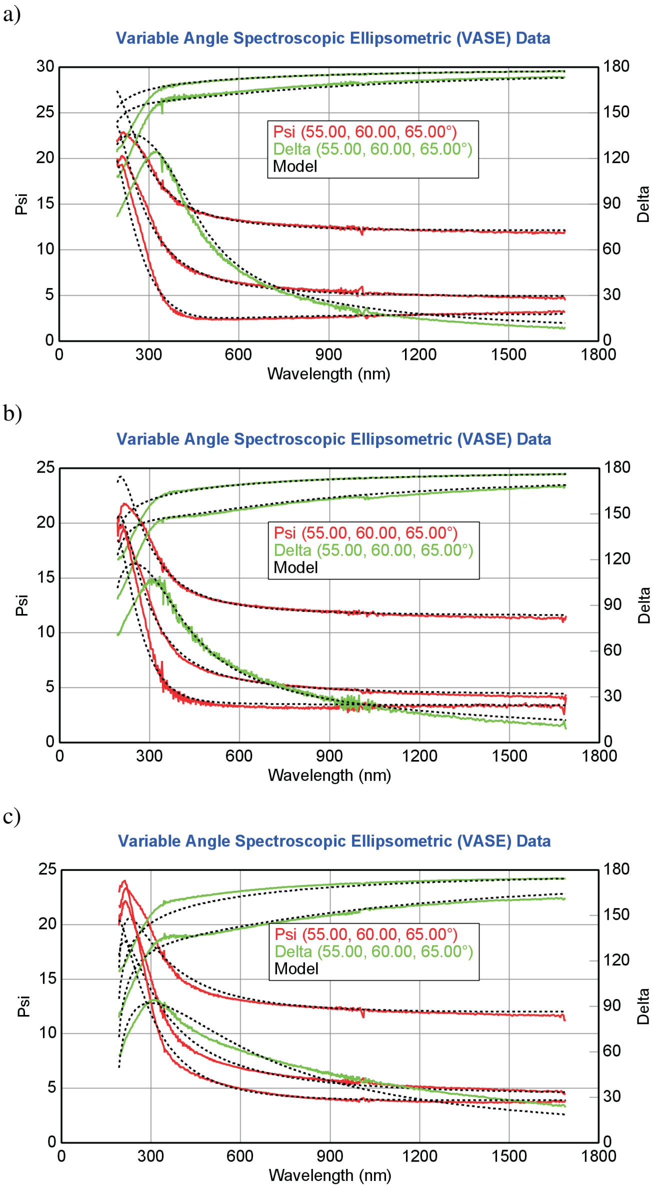

Fig. 4. Spectral dependence of ellipsometric angles Ψ and Δ measured for P1, P2, and P3 glass samples, respectively

Table 3
Values of fitted parameters

Sample number	A (n for 633 nm)	$B \times 10^{-2}$	$C \times 10^{-4}$	$K \times 10^{-4}$	roughness [nm]
P1	1.871 ± 0.119	1.946 ± 0.028	2.641 ± 0.033	0.50± 0.02	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 ± 0.0701	1.511 ± 0.023	0.348 ± 0.307	0.117 ± 0.019	16.39 ± 1.02

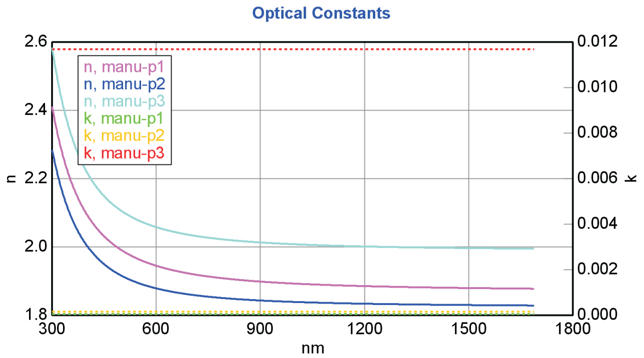

Fig. 5. Cauchy dispersion dependences of the glasses P1, P2, P3 determined for n – and k

4. Conclusions

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 concentration of PbF_2 [14]. It has been proved, that admixture of ions Yb^{3+} and Tm^{3+} results in appearance of exothermal effect related with PbF_2 crystallization on DTA/DCS curves. It has been observed in case of glass P2, with admixtures of ions Tm^{3+}, that crystallization process is run in two phases; within temperature range 400–600°C. Tellurium oxide TeO_2 is a crystallization phase at the temperature 553°C, whereas, the heat treatment of this glass at 620°C causes appearance of another low-phonon energy crystallization phase 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 displacement of the glassy state transformation temperature towards higher levels, and lowered values of parameters of thermal stability $\Delta T = T_{\text{kFigt.}} - T_g$, indicate for the improvement of the glass tendency for fluoride phase crystallization.

Refraction indexes of tellurite glasses reach very high values, of over 1.85, within all measured spectral range. The ellipsometric examinations have proved, that ions of rare earth elements, i.e. Tm $^{3+}$ and Yb^{3+}, and PbF_2 concentration have considerable influence onto changes of refractive index of basal glass P1 (without RE admixture). Doping Tm^{3+} ions to tellurium matrix of glass from the system TeO_2-WO_3-PbO-PbF_2-Na_2O results in reduction of refractive index with about 0.03 (glass P2), however, doping with Yb^{3+} ions (glass P3) results in its considerable raise (with about 0.12 within visible range) with respect to base glass P1. Doped tellurite glass has also bigger roughness, whereas, highest influence onto roughness raise, was observed in case of the glass doped with Yb^{3+} ions.

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

REFERENCES

[1] L.M. Fortes, L.F. Santos, M.C. Gonçalves, and R.M. Almeida, "Preparation and characterization of Er^{3+}-doped TeO_2-based oxyhalide glasses", *J. Non-Cryst. Solids* 324, 150–158 (2003).

[2] J. Wasylak and M. Reben, "A new oxyfluoride tellurite glasses for optoelectronics", *Eur. Glass Technology – Eur. J. Glass Science and Technology: Physics and Chemistry of Glasses* 48 (4), 264–250 (2007).

[3] D.Dorosz, "Rare erth ions doped aluminosilicate and phosphate double cald optical fibers", *Bull. Pol. Ac.: Tech.* 56 (2), 103–112 (2008).

[4] T. Kosuge, Y. Benino, V. Dimitrov, R. Sato, and T. Komatsu, "Thermal stability and heat capacity changes at the glass transition in K_2O-WO_3-TeO_2 glasses", *J. Non-CFigt. Solids* 242, 154–164 (1998).

[5] D.W. Hall, M.A. Newhouse, N.F. Borrelli, W.H. Dumbaugh, and D.L. Weidman, "Nonlinear optical suscettilibilities of some Ge-Se-Te glasses", *J. Non-Cryst. Solids* 103, 179–194 (1988).

[6] E.M. Vogel, M.J. Weber, and D.M. Krol, "Nonlinear optical phenomena in glass", *Phys.Chem. Glasses* 32, 231–253 (1991).

[7] M. Reben, J. Wasylak, and D. Dorosz, "Tellurite glasses for optical fibres fabrication", *Proc. SPIE, Int. Society for Optical Engineering* 7120, CD-ROM (2008).

[8] M. Reben, J. Wasylak, and P. Wantuch, "Optical properties and thermal stability of tellurite glasses", *Polish Conf. PKO* 1, CD-ROM (2009), (in Polish).

[9] R.M.A. Azzam and N.M. Bashara, "Spectroscopic ellipsometry data analysis:measured versus calculated quantities", *Thin Solid Films* 313–314, 33–39 (1998).

[10] F. Lahoz, I.R. Martín, U.R. Rodríguez-Mendoza, I. Iparraguirre, J. Azkargorta, A. Mendioroz, R. Balda, J. Fernández, and V. Lavín, "Rare earths in nanocrystalline glass-ceramics", *Optical Materials* 27, 1762–1770 (2005).

[11] G. Liao, Q. Chen, J. Xing, H. Gebavi, D. Milanese, M. Fokine, and M. Ferraris, "Preparation and characterization of new fluorotellurite glasses for photonics application", *J. Non-Crystalline Solids* 355, 447–452 (2009).

[12] F. Urbach, "The long wavenlength of photographic sensitivity and of the electronic absorption of solids", *Phys. Rev*. 92, 1324 (1953).

[13] D.A.G. Bruggeman, "Berechnung verschiedener physikalischer konstanten von heterogenen substanzen", *Ann. Phys*. B 24, 636–674 (1981).

[14] L. Lin, G. Ren , M. Chen, Y. Liu, and Q. Yang, "Study of fluorine losses and spectroscopic properties of Er^{3+} doped oxyfluoride silicate glasses and glass ceramics", *Optical Materials* 31, 1439–1442 (2009).