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Investigations of tellurite glasses for optoelectronics devices

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The goal of the work was to characterize and synthesize tellurite glasses from the TeO_2–WO_3–PbO–La_2O_3 system. The effect of lanthanum oxide content on the tendency to the crystallization of glassy matrix was investigated. Differential thermal analysis DTA/DSC, XRD measurement were considered in terms of the lanthanum oxide influence. Presented work is a continuation of investigations of tellurite glasses with use of the Faraday effect method. The Faraday effect is a rotation of polarization of linearly polarized light in an isotropic transparent material under the magnetic field. It has been stated that the addition of lanthanum to tellurite glass from the TeO_2– WO_3–PbO system hinders the crystallization process of glass which is very important during fiber drawing. Tellurite glasses have physical and chemical properties that make this class of materials a potential candidate in different applications, such as electrochemical and optoelectronic devices. In the field of photonics these glasses may be used as precursors for infrared fibers or windows due to the possibility of changing their phonon energies and therefore the domain of wavelength transparency as a function of compositions.

Keywords: tellurite glass, magneto-optic properties, Faraday effect, Verdet constant.

1. Introduction

TeO_2 based glasses are of great interest for use in optical communication system. The refractive index of tellurite glass from TeO_2–WO_3–PbO system reaches the value of up to 2.30 [1]. Their highest refractive indices among oxide glass in the visible and near IR region cause that the TeO_2 based glass systems are the most promising materials in optoelectronical devices [2]. The relatively high refractive index is a consequence of high polarizability of tellurium ions. Due to the same reasons, they also possess large third order non-liner optical susceptibilities, which are about 100 times higher than in case of traditional silicate glass [3–5]. The tellurium containing glasses do not show glass forming properties contrary to the silica, borate, phosphate or germanate glasses [6]. The TeO_2 is not a typical glass former. It does not form a glass by itself, but it requires the presence of other components to form a glass [7, 8]. There are five different crystalline phases: α-TeO_2, WO_3, $x TeO_2\, y PbO$, $PbWO_4$, and unidentified composition in the TeO_2–WO_3–PbO glass system, and the structure of tellurite glass does not display significant changes with variations of the compositions. Glasses of the TeO_2–WO_3–PbO system are diamagnetic materials and have the Verdet constant V ranging in 0.08–0.11 $\mathrm{min Oe^{-1}}$ for $\lambda = 633$ nm. Properties of tellurite glasses in the range of magneto-optics phenomena are very interesting for optoelectronics [1]. The Faraday rotation has a practical application in optical isolators. An optical isolator is a device that allows light to go through in one direction but severely attenuates the reflected light propagating in the opposite direction. Modern ultra-high field permanent magnets and special paramagnetic glasses have made these devices quite small, but not cheap. The combined effect of the special glass and the large magnetic field rotates the polarization plane of the light of 45° in each passage. Optical isolators have important applications in telecommunications, preventing reflected signals on fiber optic cables from producing unwanted signals. The isolators are important when lasers are used because reflected light can cause a havoc with the operation of the laser itself [9].

2. Experimental

Tellurite glasses were obtained by melting 100 g batches in a gold crucibles in an electric furnace at the temperature 850 °C in air atmosphere. The melts were poured out into a steel form. The glasses prepared in such a manner were thermoannealed at 350 °C for 12 hours. The following raw materials were used to prepare the batches: TeO_3, WO_3, PbO and La_2O_3. The compositions of the glasses are listed in Tab. 1.

The ability of the obtained glasses to crystallize was determined by DTA/DSC measurements conducted on the Perkin–Elmer DTA-7 System operating in the heat flux DSC mode. The samples (60 mg) were heated in platinum crucibles at a rate of 10 $\mathrm{°C\,min^{-1}}$ in dry nitrogen atmosphere to the temperature of 1000 °C. The glass transition temperature T_g was determined from the inflection point on the enthalpy curve and calculated using the 7 Series Perkin–Elmer Thermal Analysis Software Library. The kind of the formed crystallites were examined by XRD (Philips X'Pert

T a b l e 1. Composition of the melted tellurite glasses.

	Chemical composition [mol%]			
Glass No.	TeO_2	WO_3	PbO	La_2O_3
0	60	30	10	—
A	59	30	10	1.0
B	58	30	10	2.0
C	57	30	10	3.0

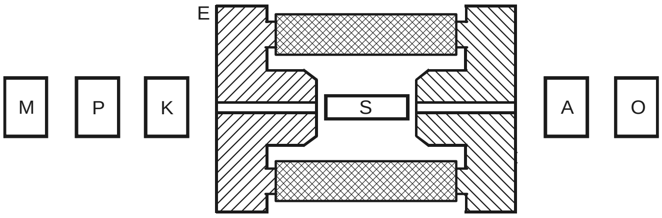

Fig. 1. Schema of measuring system to investigation of Faraday effect: M – monochromator, P – polarizer, K – semishadow plate, E – electromagnet, S – sample, A – analyser, O – ocular.

Diffractometer) method. The density of glasses was determined by the method of hydrostatic weighing.

The experimental of the method probing the Faraday effect was carried out in a magnetic field with an induction of $B = 0.06$ T. The measurements of steering angle were executed in the range from 500 to 650 nm. From the value of the rotation of the polarization plane, the value of Verdet constant was estimated.

From the samples of different percentage of La_2O_3, the one with the optimum composition assuring the best physical and chemical properties, was chosen to be compared with the samples without La_2O_3 addition. The block diagram of measuring system and measuring apparatus to investigate the Faraday effect are given in Fig. 1.

3. Results and discussion

The results of the thermal analysis of the 0, A, B and C glasses are shown in Fig. 2. Analysis of DTA/DSC curve of glass No. 0 shows the thermal effects characteristic for typical phase transitions occurring in a glassy material and a very strong exothermic peak near 545 °C. Therefore, this glass was selected for heat treatment at the 545 °C for 1 h. The XRD method showed the presence of two crystalline phases (TeO_2 and WO_3) in the glass No. 0 heated at 545 °C for 1 h (Fig. 3). Analysis of DTA/DSC

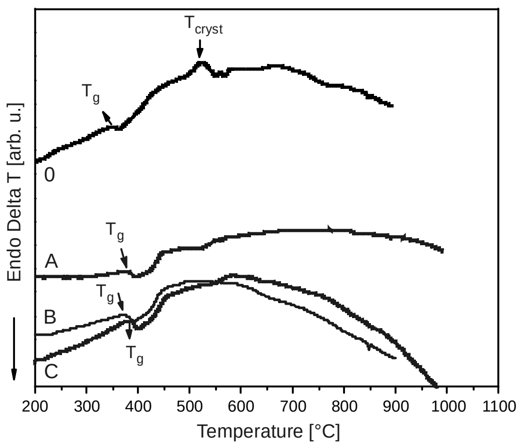

Fig. 2. DTA curves of glasses 0, A, B, C.

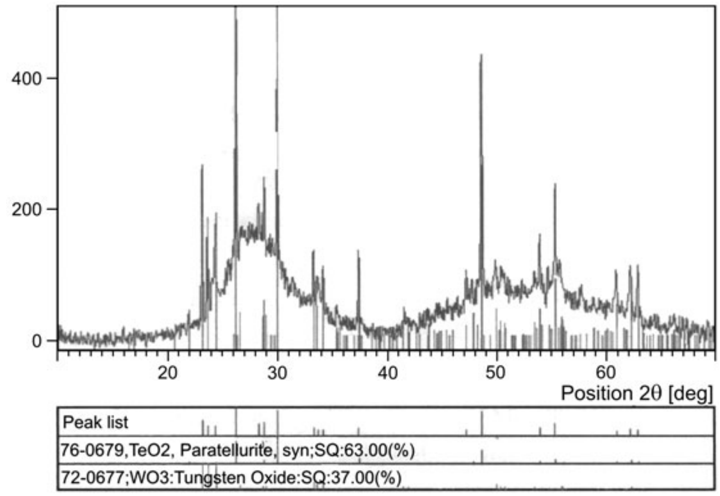

Fig. 3. XRD pattern of glass 0.

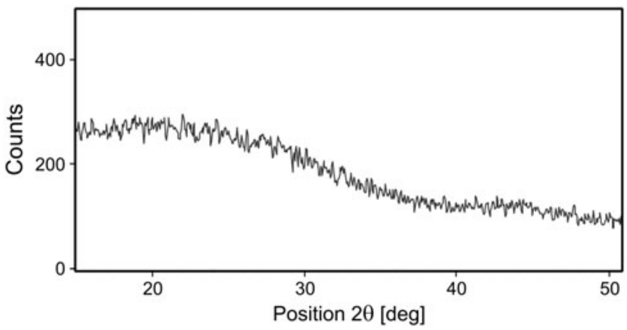

Fig. 4. XRD pattern of glass A.

curves of glasses from the system TeO_2–WO_3–PbO doped with lanthanum oxide indicates the presence of a well visible effect of the glassy state transformation, while the exothermal effect, connected with the crystallization of TeO_2 and WO_3, was not observed (Fig. 2). The XRD analysis confirms that glass is amorphous (Fig. 4).

Generally, the addition of La_2O_3 content in glasses from the system TeO_2–WO_3––PbO causes an increase of the transformation temperature to 391 °C and the increase of the specific heat (ΔC_p) accompanying the glass transition region, which may be evidence for an increased flexibility of the glass network. The obtained glasses have a good thermal stability (Tab. 2). Glasses A, B, C do not show a tendency to crystallization. It can be concluded that the presence of lanthanum ions in the glass structure decreases the tendency to crystallization.

T a b l e 2. Thermal characteristics of tellurite glasses with La_2O_3.

Glass No.	T_g [°C]	ΔC_p [$Jg^{-1}°C^{-1}$]	$T_{max\ cryst.}$ [°C]	$\Delta H_{cryst.}$ [Jg^{-1}]	Crystallizing phases
0	363	0.148	545	2.560	TeO_2, WO_3
A	371	0.187	—	—	—
B	384	0.302	—	—	—
C	391	0.477	—	—	—

T_g – glass transition temperature, $T_{max\ cryst.}$ – maximum of crystallization temperature, ΔC_p – specific heat accompanying the glass transition, $\Delta H_{cryst.}$ – enthalpy of crystallization.

Tellurite glasses from the TeO_2–WO_3–PbO system possess high transparency in the visible and IR spectral range (up to 5.5 μm), low dispersion and high refractive index (1.85), which is a consequence of the high polarizability of tellurium ions. An addition of La_2O_3 into the glass structure causes an increase of refractive index up to 2.0. Figure 5 shows an example of the transmittance spectrum of the C glass. It may be seen that these glasses have quite a wide transmission window. It should be also noted that among oxide glasses, tellurite glasses have small maximum vibrational frequencies, good corrosion resistance and mechanical stability. The density of the obtained glasses depends on the glass composition. It slightly increases with addition of La_2O_3 for the glass without La it is 6.45 g/cm^3, while for glasses A, B, C it ranges from 6.56 up to 6.82 g/cm^3.

The value of the turn angle of the plane of polarization without magnetic field was calculated for sample 0 and C. The maximum value of the turn angle of the plane of polarization decreases with La_2O_3 addition into the glass structure (for glass 0 equal to 5°36' and for glass C – 1°36'). For the glass 0 the dependence of the turn angle of the plane of polarization on the light wavelength under magnetic field was not

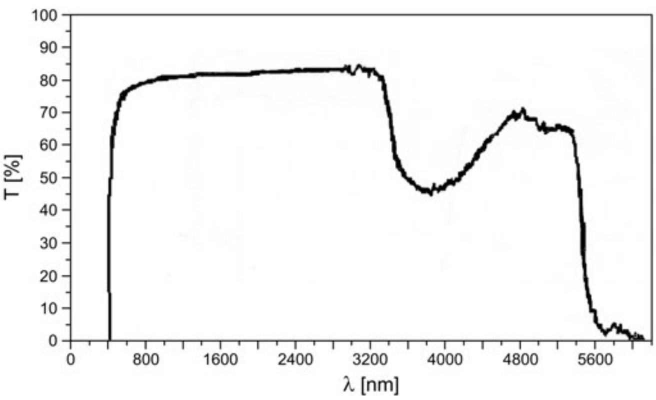

Fig. 5. Transmittance of glass from the TeO_2–WO_3–PbO–La_2O_3 system.

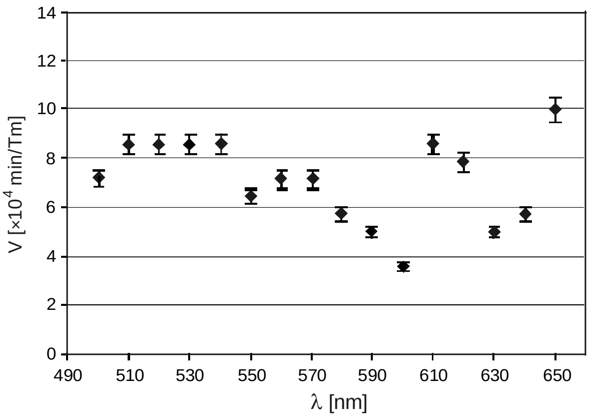

Fig. 6. The dependence of turn angle the plane of polarization from wavelength in constant magnetic field of induction 0.06 T for tellurite glasses lanthanum ions doped.

observed. In case of glass C the investigation showed the dependence of turn angle of the plane of polarization and the Verdet constant on magnetic field induction for the range of wavelength 490–650 nm (Fig. 6). The maximum value of the turn angle was received for the wavelength $\lambda = 650$ nm. Calculating for this wavelength the Verdet constant gives the value of 10×10^4 min/Tm. The well visible Faraday effect in glass C is connected with La_2O_3 addition.

4. Conclusions

Thermal analysis method (DTA/DSC) is a simple and very sensitive method which enables to investigate the crystallization processes in glasses and shows the thermal effects characteristic for typical phase transitions occurring in a glassy material. From the thermal investigation it can be concluded that ability to crystallization of tellurite glasses strongly depends of La_2O_3 content. When lanthanum ions are added to the TeO_2–WO_3–PbO glass system, the crystallization effect does not appear. XRD investigation confirms appearance of two crystalline phases (TeO_2 and WO_3) in the glass No. 0 (without La_2O_3 addition) but on the other hand it confirms that in case of glasses A, B, C the peaks connected with presence of crystalline phases are not observed.

The magnetooptical properties are observed in the TeO_2–WO_3–PbO glass system thanks to La_2O_3 addition, it has been confirmed by a Faraday effect occurrence. The polarization of the glass is not only the result of electron polarization but also includes the contribution of the orientation of charged defects in glass. Those phenomena have influence on calculated Verdet constant.

Thanks to the addition of La ions into the tellurite glass structure, those glass systems can be considered as a promising material for an application in magneto-optic devices. For further application of tellurite glasses as optical shutters and optical modulators, a dynamic method will be proposed to monitor the Faraday effect.

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