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# Magneto-optical properties of high-purity zinc-tellurite glasses

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ABSTRACT

High-purity $TeO_2$–ZnO, $TeO_2$–ZnO–$Na_2O$ and $TeO_2$–ZnO–$La_2O_3$–$Na_2O$ glasses have been characterized in terms of material applicability for magneto-optical devices. Glasses with extremely low content of absorbing impurities of 3d-transition metals and hydroxyl groups have been prepared inside a sealed silica glass chamber in a flow of purified oxygen. Magneto-optical properties, including spectral dependence of the Verdet constant in the 450–1561 nm range and magnetic figure of merit, crystallization stability and optical properties in the IR range were studied.

## 1. Introduction

Bulk and fiber devices using the Faraday effect, such as rotators and isolators, are important components of laser systems. They allow controlling radiation polarization, creating multipass generation schemes, and transmit radiation in a needed direction. Application of these devices in optical laser schemes operating at different wavelengths and with different beam apertures demands magneto-optical active elements with a broad emission spectrum and large aperture. For fabricating bulk devices, crystalline materials are used traditionally. However, it is a rather complicated and costly task to grow a crystal of large size and high quality. Ceramics and glasses possessing merits such as isotropy of properties, low cost, relative simplicity of synthesis and fabrication of optical elements of high optical quality may be alternative materials. The most important merit of glass-like materials is a feasibility of producing magneto-active fiber optical waveguides of different types [1–5] and bulk optical elements [3,4,6]. Such devices may be used for fabricating magneto-optical Faraday rotators and isolators and magnetic and electric field sensors, modulators, switches, and fiber-optic Bragg gratings. Thus, glasses must have a rather high value of Verdet constant, good mechanical strength, wide transmission spectral band and low optical losses. One of the types of such magneto-active glasses is $TeO_2$-based glass doped by other oxides that has a wide transmission spectral band 0.4–5.5 μm. The value of the Verdet constant of tellurite glasses could be modified by changing the concentration of Zn, Mo, W and La oxides [7–10]. Long enough bulk samples of crystallization-stable tungstate-tellurite and zinc-tellurite glasses containing sodium, lanthanum, molybdenum and bismuth oxides as modifying components with low optical losses have been obtained [11]. The possibility of fabricating high-purity tungstate-tellurite and zinc-tellurite large bulk, striae-free samples of glass shaped as cylinders having a diameter of 8–12 mm and a length of 90 mm was demonstrated [8,12], also, massive zinc-tellurite optical elements could be produced [6].

As was mentioned above, one of the important requirements for optical materials is a wide transmission band and a low content of impurities. Application of source reagents of special purity and dedicated dehydration procedure permitted attaining extremely low total impurity content of 3d-transition metals (0.2–2 ppm wt), absorption by hydroxyl groups (0.001–0.002 $cm^{-1}$ near the band maximum of ~3 μm) and, hence, low optical losses. Low optical losses on absorption in bulk samples determined by laser calorimetry were less than 200, 90 and 100 dB/km at the wavelengths of 1.06, 1.56, and 1.97 μm, respectively. Scattering losses determined by laser ultramicroscopy were low and reduced critically with increasing wavelength. In addition, tellurite glasses are very good candidates for applications in fiber optics. Step-index optical fibers with low optical losses as well as microstructured fibers for supercontinuum generation were successfully fabricated from tellurite glasses [9,13–15].

Also, thanks to the negative value of thermooptical constant $Q$ [16] optical elements made of tellurite glass may be used in compensating of thermally induced depolarization schemes without using a reciprocal quartz rotator [17], that allows simplification and size minimization of the optical scheme. Also, high-aperture optical elements made of this type of glass [6] allow using them in optical systems that operate with high-aperture beams.

The value of the Verdet constant of the tellurite glasses with various compositions were previously studied for the 550–950 nm range [1]

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and for the 700–1060 nm range [18]. Also, typical values of the Verdet constant of tellurite glass are presented in papers for bulk [4] and fiber [19] materials. Changing the composition of the glass sample allow to slightly change the value of the Verdet constant [1]. Thus it is important to produce high-purity glasses with wide transmission band and measure their characteristics to use them as the material for optical devices.

In this work several samples of the high-purity zinc-telluride glasses were fabricated and characterized. A number of their characteristics such as transmission spectra, content of absorbing impurities of 3d-transition metals and hydroxyl groups, the wavelength dependence of the Verdet constant in the 450–1561 nm range and the theoretical dependence of the diamagnetic part of the Verdet constant were studied. The results obtained show that high-purity zinc-tellurite glasses with modifying additional components could be used as the material for creating magneto-active optical elements.

## 2. Experiment

Glasses of $75TeO_2$–$25ZnO$ (TZ), $77.1TeO_2$–$12.5ZnO$–$10.4Na_2O$ (TZN), $74TeO_2$–$12ZnO$–$4La_2O_3$–$10Na_2O$ (TZLN-1), and $73TeO_2$–$13ZnO$–$4La_2O_3$-$10Na_2O$ (TZLN-2) compositions (mol%) were produced by melting the batch in platinum crucibles inside a sealed silica chamber in the atmosphere of purified oxygen [11].

High-purity starting materials: oxide of tellurium $TeO_2$ produced by the original patented method [20], oxide of zinc ZnO produced by diethyl zinc oxidation reaction, commercially available lanthanum oxide $La_2O_3$ and sodium carbonate were used for preparation of the glasses. The impurity content in the initial oxides and glasses was determined by different variants of atomic emission analysis: analysis in direct current arc, with inductively coupled plasma, and with chemical preconcentration of impurities. The total content of 3d-transition metal impurities in the mixture of initial oxides did not exceed 0.2–2 ppm wt and the total concentration of rare-earth elements was less than 1–2 ppm wt [8,12]. The concentration of impurities remained at the same level during glass synthesis as in the previous studies, which indicated that the synthesis by means of the used technique did not result in significant contaminations [21].

Glasses were melted at 800 °C for several hours with recurrent stirring of the melts until they attained the concentration of water vapors in oxygen $\sim 5 \times 10^{-5}$ mol% (the dew point was $\sim -80$ °C) at the reactor output. Then the melt was poured into silica glass moulds and annealed for several hours at glass transition temperature. After annealing the obtained samples were extracted from the moulds and mechanically processed for further investigations. Thus, cylindrical samples with the good optical quality, with 10–12 mm in diameter, 2.6 and 10 mm thick were obtained.

The visible spectrum was recorded by the spectrophotometer Lambda 900 and the IR spectrum was recorded by the IR Nicolet 6700 Fourier spectrometer. Absorption coefficient was calculated from transmission spectra data using the Beer–Lambert–Bouguer law: the absorption coefficient $\alpha = -\ln(I / I_0) / L$, where $L$ is sample length. The NETZSCH STA - 409 PC Luxx instrument was used for investigations by differential scanning calorimetry. Measurements were made in argon flow with flow rate of 60 ml/min, at the heating rate of 10 K/min within the temperature range of 200–700 °C. The samples were in the form of discs with diameter of ~5 mm, and mass of about 30 mg. The accuracy of the measurement was estimated to be ± 3 °C.

The dependence of the Verdet constant on wavelength was studied using the scheme presented in Fig. 1. The scheme comprised calcite wedge (1), radiation absorber (2), magnetic system (3), sample (4), Glan prism (5), and CCD camera (6). Diode lasers at the wavelengths of 450, 531, 633, 810, 980, 1064, 1310, and 1561 nm were used as sources of probe laser radiation.

The linear polarized probe radiation after the calcite wedge propagated through the sample placed in the magnetic system based on

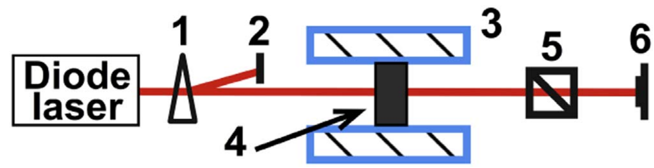


**Fig. 1.** Scheme of the experiment.

Nd-Fe-B magnets. Before installing the sample, the Glan prism was cross-polarized relative to the calcite wedge. The angle of polarization rotation $\phi$ was measured by rotating Glan prism to achieve minimal signal at the CCD camera while the sample was located in the magnetic system (Fig. 1). For studying the temperature dependence of the Verdet constant, sample (4) and magnetic system (3) were placed in a cryogenic vacuum chamber, where the sample was cooled by liquid nitrogen down to 80 K.

## 3. Results

### 3.1. Thermal properties

Thermal effects in glass were studied by the differential scanning with heating rate of 10 °C/min. Thermograms of the prepared glasses are presented in Fig. 2.

The glass transition temperatures $T_g$ are 298, 264 and 330 °C for TZLN-1, TZN and TZ glass respectively. Thermograms of TZN and TZ glass are characterized by thermal effects of crystallization and crystal melting. The temperatures at the start of crystallization $T_x$ is ≈ 440 and 400 °C for TZ and TZN glass respectively.

### 3.2. Transmission spectra and hydroxyl groups absorption

Fig. 3(a) presents the visible and near IR parts of transmission spectra of TZLN-1 and TZLN-2 samples, which are typical for all the glasses studied.

The zinc-tellurite glasses with modifying additions of lanthanum and sodium oxides have high transparency in the visible and near-IR regions; the short-wave transparency edge for all studied glass compositions is located in the range of 350–400 nm (Fig. 3(a)). The absence of characteristic absorption bands of 3d-transition metals and rare-earth elements in the presented wavelength region confirms the low content of the impurities. The absorption band of dissolved platinum with maximum near 400 nm, which appears in the case of platinum crucibles

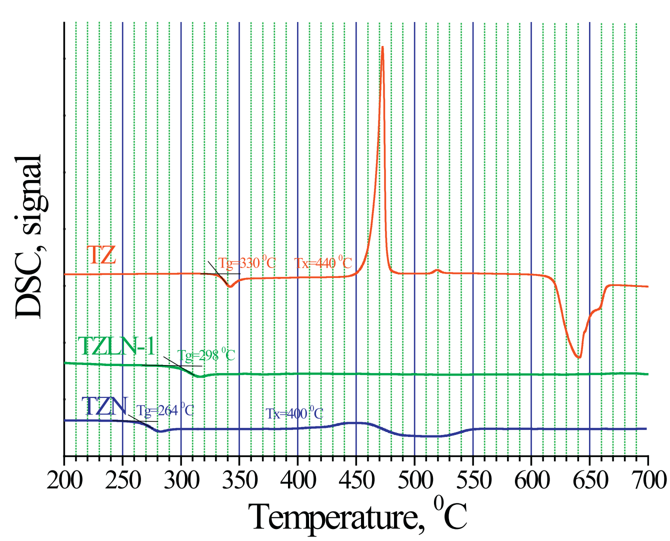


**Fig. 2.** Thermograms of differential scanning calorimetry of zinc-tellurite glasses (heating rate of 10 °C/min).