Original Article

Controlled formation of metallic tellurium nanocrystals in tellurite glasses using femtosecond direct laser writing

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ABSTRACT

Tellurite glasses are considered a potential alternative for applications not achieved by SiO2-based glasses, presenting interesting optical properties, such as high linear and nonlinear refractive indexes, extended optical window, being also suitable for metallic nanoparticle growth, like Te0. When doped with sulfide species, it can benefit the reduction of Te4+ to Te0, which can be advantageous to synthesize in-situ chalcogenide nanoparticles and quantum dots. This work presents investigations on the reduction of Te4+ to Te0 in tellurite glasses doped with PbS and PbO/ZnS, and aims to control this redox process through the processing with pulsed fs-laser. Tellurite glass samples were synthesized by melt-quenching technique and the thermal and structural properties were explored by different techniques, such as DSC, Raman scattering spectroscopy and mapping experiment, TEM and SAED. Reduction of tellurium to Te0 nanocrystals into tellurite glass after laser irradiation was studied in detail and confirmed by the presence of bands at ~120 and 140 cm−1 in Raman spectroscopy and mapping, assigned to the Te−Te vibrational modes, which suggest that S2− induces in-situ Te4+ reduction. Moreover, quasi spherical tellurium nanoparticles were observed through TEM and confirmed their chemical nature and crystallization by SAED. The study of tellurium reduction in the vitreous matrix becomes particularly important and promising for some applications, since its reduction generates changes in the refractive index by precipitation of Te0 nanoparticles, allowing the fabrication of waveguides and as photosensitive material for tridimensional data storage.

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1. Introduction

Among oxide glasses, silica and silicates are widely used in various photonic devices [1,2], although the exploitation of non-SiO2 oxide glass such as tellurites and phosphates are also required to overtake silicate limitations related to their phonon energy, low refractive index, low rare-earth ions solubility and high characteristic temperatures. Particularly, tellurite glass exhibits interesting optical properties such as high linear and nonlinear refractive indexes, photochromism and photoluminescence when doped with transition metals, rare-earth ions, and quantum dots, for instance [3-6]. TeO2-based glasses, depending on chemical composition, are promising matrices because of their large thermal stability against crystallization, chemical resistance, hyper-polarizability (high linear and nonlinear refractive indexes), extended optical window in the middle infrared region and low characteristic temperatures when compared to traditional silicate compositions [7]. In photonics, tellurites play an important role when doped with luminescent compounds, which enables their use for applications as optical fiber amplifiers, thermal lens, optical sensing, luminescent displays and devices, energy conversion, and so forth [8,9].

Although glasses doped with sulfide-based quantum dots, for example CdS and PbS, are widely reported in silicate and phosphate glasses upon long heat treatment at temperatures above the glass transition temperature, Tg [10-12], there is a lack of research on those quantum dots in TeO2-based glass because they can promptly suffer redox reactions, reducing from Te4+ to Te0, depending on the redox potential of the modifer or dopant compounds in the glass matrix [13]. TeO2 presents the higher reduction standard potential (+0.530), E0(V), when compared to other oxide glass forms, such as SiO2 (-0.909), P2O5 (-0.500) and B2O3 (-0.890) [14-16]. Once obtained Te0 into the network, it tends to leave the vitreous structure and clustering in the interstices through thermal diffusion process [17]. This can influence the physical properties of the sample, causing changes in characteristic temperatures, refractive index, and color, depending on the size and amount of Te0 nanocrystals [13].

The great reduction ability of Te4+ has been explored to synthesize colloidal Te0 nanowires, filters, catalyst, etc. [18]. Silva et al. synthesized Te0 nanowires from TeO2, using H3PO2 as a reducing agent [18]. Charton et al. attributed the reduction of Te4+ in the binary glass system TeO2-Sb2O3 to the presence of antimony, which acts as a reducing agent by oxidizing Sb3+ to the Sb5+ and inducing the reduction of Te4+ to Te0 [13,19].

In this sense, a strategy to promote the reduction of tellurium ions in a controlled manner in the glass matrix, and taking advantage of the relative high E0 of TeO2, is the use of fs-laser processing, which emerges as a promising way for spatially-controlled Te0 formation. Femtosecond laser processing is a promising alternative to fabricate photonic devices such as planar waveguides, interferometers, and optical data storage materials [20], and have already been reported for reduction of glass dopants, as Ag and Cu [21,22].

The fs-laser processing is based on the optical energy transfer from the laser to the material around the focal point, ionizing many atoms that, in turn, transfer energy to the network. This energy can cause a structural or phase change in the material, resulting in local refractive index change, enabling the production of planar waveguides [23]. In addition, nonlinear effects during micromachining can induce local changes in both structure and optical properties, such as absorption coefficients, refractive index [23]. Free electrons, produced from ionization due to laser interaction, can also contribute to redox reactions, especially with metallic elements susceptible to reduction, depending on their reduction potential. Such phenomenon was previously observed in oxide glasses where Cu0 and Ag0 nanoparticles were produced under fs-laser irradiation [22,24]. Thus, micromachining technique appears as an interesting alternative for direct waveguides production, without the need of thin films deposition on a support material. Another key advantage of direct femtosecond laser writing is related to the fact that such structures can be produced in the volume of the material without any damage of the surface [25,26].

Considering the interest in understanding and overcoming the obstacles for growth of chalcogenide semiconductors nanocrystals in tellurite glasses due to their darkening tendency, and to take advantage of the easy reduction of Te4+ to Te0 and formation of elemental nanoparticles, this work is devoted to the study of a tellurite glass doped with PbS and PbO/ZnS, and investigating their impact on the reduction of Te4+ to Te0. Thus, to manage the reduction of tellurium ions, we investigated the application of fs-laser micromachining for obtaining of Te0 in a controlled manner, with corresponding changes on the refractive index and sample colors (darkening effect). Tellurite susceptibility to optical properties modifications makes them promise candidate for the fabrication of planar waveguides and 3D-data storage materials [27].

2. Experimental

Tellurite glass samples with nominal composition of 98 [75TeO2-15ZnO-10Na2O], called TZN, doped with 2.0 mol% of PbS, 2.0 mol% of PbO and 1.0/1.0 mol% of PbO/ZnS were

<table>
<thead>
<tr>
<th>Sample labels</th>
<th>Molar compositions (mol%)</th>
<th>Mold temperatures (°C)</th>
<th>Glass colors</th>
</tr>
</thead>
<tbody>
<tr>
<td>TeO2</td>
<td>ZnO</td>
<td>Na2O</td>
<td>PbO</td>
</tr>
<tr>
<td>TZN</td>
<td>75</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>TZN:PbO</td>
<td>73.5</td>
<td>14.7</td>
<td>9.8</td>
</tr>
<tr>
<td>TZN:PbS</td>
<td>73.5</td>
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synthesized by the conventional melt-quenching method under room atmosphere in a covered α-Al₂O₃ crucible (Table 1). Batches of 5 g were prepared by weighing and thoroughly grinding the high purity raw materials, TeO₂ (Prichem, 99.99%), ZnO (Aldrich, 99.0%), Na₂CO₃ (Aldrich, 99.5%), PbS (Aldrich, 99.9%), PbO (Aldrich, >99.0%) and ZnS (Aldrich, 99.99%), in an agate mortar, loaded into the crucible and then melted at 800°C for 30 min. Then, the liquid was poured into a stainless-steel mold preheated at temperatures between 100 and 250°C, followed by annealing at the same temperature for 2 h to remove residual internal stress. The glass samples were cut into equal pieces using an auto diamond saw and optically polished with parallel faces for further characterizations.

The glass transition temperature (Tg) for the TZN glass samples were obtained by differential scanning calorimetry (DSC) through the method described by Varshneya [28] and determined as 280°C. The crystallization temperature (Tx), in turn, was not identified in the temperature range up to 600°C due to the high thermal stability against crystallization.

Sulfide doped tellurite glasses containing PbS or ZnS were obtained as dark-colored samples when the cooling rate is high, in other words, when the mold is preheated at temperatures between 100 and 150°C (below Tg) and presented low mechanical resistance due to thermal shock. On the other hand, when the mold is preheated at temperatures close to Tg, that is, at 250°C, light yellowish samples can be obtained. This behavior probably originates from complex redox equilibria in the liquid state, which are frozen in different states depending on the cooling rate, leading to the formation of dark samples when doped with sulfide species. To investigate the origin of the darkening effect on glass samples, transmission electron microscopy and Raman spectroscopy were employed to study the following tellurite glass compositions as shown in Table 1.

For the localized reduction of Te⁴⁺, yellowish samples were irradiated using a femtosecond laser (Femtosource XL) operating at 800 nm, with pulse duration of 50 fs and repetition rate of 5 MHz. The laser beam with average power of 150 mW was focused close to the sample surface with a 40x objective lens (NA = 0.65). Sample was moved in the XY plane perpendicularly to the beam, at constant speed of 0.1 mm s⁻¹, as resumed in Fig. 1. For those experimental conditions, the peak intensity is estimated to be ~17 TW/cm² and laser fluence of 64 kJ/cm² (considering 150.000 pulses-per-spot and spot diameter of ~3 μm). Direct laser writing was performed in an area of 9 mm², with 3 mm long lines, spaced by 0.04 mm.

3. Results and discussions

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Fig. 2 presents the Raman spectra of glass samples related in Table 1 and references TeO2 and TeO. Tellurium oxide paratellurite \( \alpha \)-TeO2 is built from linear chains of [TeO4] units arranged in a trigonal bipyramidal geometry, presenting four strong bands at 643 cm\(^{-1}\) and 393 cm\(^{-1}\), assigned to Te\(\alpha\)–O symmetric and asymmetric stretching and at 147 cm\(^{-1}\) and 119 cm\(^{-1}\), assigned to bending modes of TeO4 units in a 3D-network [8]. Standard TeO spectrum exhibits three main bands in the frequency range from 75 to 160 cm\(^{-1}\), assigned to tellurium-brushing vibrations between tellurium and non-binding oxygen in TeO2 and TeO3,1 units [30,31]. It is worthy to note that for samples TZN: PbO and TZN: PbS, both containing 2 mol% of Pb atoms, the band centered at 750 cm\(^{-1}\) is more intense than that at 660 cm\(^{-1}\), while the band assigned to ZnO–Zn and/or TeO–Te symmetric deformation is localized between 390 and 500 nm and does not change in intensity [32]. The inverse ratio is observed for lower Pb content in samples TZN and TZN: PbO/ZnS, indicating that the addition of Pb precursors above 1 mol% promotes a slightly structural glass network modification by increasing the amount of more connected trigonal bipyramidal units [TeO4], decreasing the conversion to [TeO3] and [TeO3,1] units, prevailed in samples TZN: PbO and TZN: PbS [8].

Fig. 3 presents the baseline corrected and normalized Raman spectra for glasses and TeO reference in the frequency range from 75 to 160 cm\(^{-1}\). Raman spectra of sulphide-free samples, TZN and TZN: PbO, do not exhibit signals assigned to TeO, indicating that tellurium preferentially stays in a fourfold oxidation state during the glass synthesis, forming a glass network based on [TeO4] units, and regardless of the cooling rate, visible transparent yellowish glass samples are obtained. On the other hand, the spectra of sulfide containing samples, TZN: PbS and TZN: PbO/ZnS, presented two narrow bands centered at 119 and 138 cm\(^{-1}\), and at 120 and 139 cm\(^{-1}\), respectively, which are assigned to metallic Te and attributed to the transverse and longitudinal stretching between tellurium atoms in their hexagonal crystalline structure [33]. Combining the fact that TZN: PbS and TZN: PbO/ZnS samples were obtained applying a rapid cooling rate (preheated mold at 100 °C), resulting in dark brownish samples with the appearance of TeO Raman bands assigned to TeO, one should suggest that Te4+ ions are involved in a complex redox equilibrium which leads to the in-situ and uncontrolled formation of reduced Te species into the glass network during the synthesis process (melting and cooling steps).

Comparing the maximum intensities of Raman bands assigned to the vibrational modes of TeO centered at 114 and 135 cm\(^{-1}\) with the Raman bands identified between 100 and 150 cm\(^{-1}\) in samples TZN: PbS and TZN: PbO/ZnS, a shift to higher energies of 6 and 4 cm\(^{-1}\) in sample TZN: PbS and 5 and 3 cm\(^{-1}\) in sample TZN: PbO/ZnS is detected and could be attributed to the presence of hyperpolarizable Te atoms in [TeO4] units, because of the formation of highly polarizable TeO bonds and the high electronic density due to the lone electron pair of Te4+ [34]. Different from Te–Te linkages in TeO macrocrystals (standard sample), Te–Te bonds in TeO nanocrystals, grown inside the tellurite glass, feel a different medium polarizability provided by the higher polarizable structures of [TeO3] units, resulting in the shifting to higher energies of the maximum Raman band intensities [35].

As mentioned before, Te4+ from [TeO4] units have a relatively high standard reduction potential, \( E^0(V) \), when compared to other glass former, such as GeO2 and SiO2, for example, with potentials of \(-0.145 \) and \(-0.909 \) V, respectively [14]. Considering the formation of free sulfide ions (S2−) during the glass melting, they may act as reduction agent of tellurium ions, contributing to the formation of reduced tellurium species TeO during the glass synthesis in the liquid state. The uncontrolled formation of such tellurium reduced species leads the nucleation and growth (clustering) of TeO nanoparticles, which is in accordance with the spontaneous reduction process suggested by the following semi- (Eqs. (1) and (2)) [14,15] and global (Eq. (3)) reactions for the proposed redox equilibrium.

\[
\text{S}_2^2^- \rightarrow \text{S}^0 + 2e^- \quad E^0 = +0.407 \text{ V} \quad (1)
\]

\[
\text{TeO}_2 + 4e^- \rightarrow \text{Te}^0 + 2\text{O}^2^- \quad E^0 = +0.530 \text{ V} \quad (2)
\]

\[
\text{TeO}_2 + 2\text{S}_2^2^- \rightarrow 2\text{S}^0 + \text{Te}^0 + 2\text{O}^2^- \quad E^0 = +0.937 \text{ V} \quad (3)
\]

To confirm the formation of TeO nanocrystals promoted by the presence of S2− in the melt and frozen after rapid quenching, TEM was performed and presented in Fig. 4. As can be seen, in agreement with the presence of Raman bands assigned to different Te–Te stretching, spherical nanoparticles homogeneously distributed in the glass matrix with particle sizes varying from 20 to 40 nm were detected. In order to determine the nanocrystals chemical nature, selected-area electron diffraction pattern was extracted from a rich-nanocrystal region, as shown in Fig. 5a for the samples TZN: PbS. Fig. 5b resumes the XRD for an indexed (ICSD 040042) and a standard sample of hexagonal metallic Te, showing...
their main crystallographic planes (101), (012) and (021). From SAED pattern, the diffraction angles 2θ of sample TZN:PbS were determined through measurements of the white spot distances aided by the PTC Lab® software. Thus, the calculated values were converted into real distances (in nm) and, finally, the 2θ values were obtained and compared with the indexed Te⁰ X-ray pattern. Therefore, comparing the diffraction peaks, it is clearly observed a superposition of 2θ angles at 27°, 38° and 49°, assigned to the planes (101) (012) and (021) of hexagonal Te⁰ crystalline phase. The highest intensity (101) plane present an interplanar distance (d_{hal}) of 0.32 nm, followed by the (012) plane, in accordance with the SAED data. This result, as already suggested by Raman data, supports the formation of Te⁰ nanocrystals during glass melting, contrary to the absence of Raman bands related to Te⁰ stretching in the yellowish samples.

Confronting the TEM images, SAED pattern and Raman spectra, the results indicate the formation of Te⁰ nanocrystals

![TEM images](image1.png)
from reduction of Te$^{4+}$ promoted by the presence of S$^{2-}$ species (redox equilibrium happening in the liquid state — melting step — and frozen due to the rapid cooling), also evidenced by the darkening effect observed in the samples TZN:PbS and TZN:PbO/ZnS when fast cooling rate is applied.

3.2. fs-laser processing

To control the formation of Te$^0$ in the yellowish samples TZN:PbS and TZN:PbO/ZnS obtained at lower cooling rate (mold at 250 °C) and free of metallic Te nanoparticles, the fs-laser micromachining technique was used to allow the generation of free electrons in the glass volume by nonlinear optical interactions [20,22]. A yellowish TZN:PbS sample was irradiated using a scanning speed of 0.1 mm s$^{-1}$ and laser power of 150 mW, resulting in an engraving area of 9 mm$^2$ (3 mm × 3 mm), as illustrated in Fig. 6a. The engraved area contains laser-written lines separated by 40 μm of each other obtained right below the glass surface (Fig. 6b). The UV–vis absorption spectra of the non-irradiated (NIA) and laser-irradiated areas (LIA) are shown in Fig. 6c, which show a slight increase in the absorption of the irradiated area (LIA) in the visible range, also confirmed by the sample darkening observed in Fig. 6a. Moreover, the electronic absorption edge occurs at around 400 nm for the non-irradiated and irradiated region. In order to better visualize the changes caused by laser irradiation, the inset in Fig. 6c, shows the ratio between both spectra LIA/NIA. One can observe an increase of absorbance around 630 nm, which can be related to surface plasmon resonance of metallic tellurium nanoparticles [36].

When comparing the absorption spectra of the non-irradiated area (NIA) with the laser-irradiated area (LIA), one should note that the UV cut-off related with the bandgap energy takes place at the same wavelengths. In other words, direct laser writing (DLW) does not modify the glass structure and, hence, it does not change the overall bandgap energy. On the other hand, the absorption coefficient of LIA progressively increases from the near infrared to the UV–visible range.

Fig. 6 – (a) Photograph of the (II)TZN:PbS sample after fs-laser irradiation and (b) optical microscopy of fs-laser irradiated area considering a 200 μm scale; (c) UV–visible absorption spectra of (II)TZN:PbS sample in irradiated (LIA) and non-irradiated areas (NIA). The inset shows the ratio between LIA and NIA spectra.

Fig. 7 – Raman spectra of TZN:PbS yellowish sample after fs-laser irradiation obtained from the scattering of NIA and LIA in comparison of Te$^0$ standard sample.
when compared to NIA. Such behavior is characteristic of light scattering mechanisms by small scattering centers with average sizes comparable with the incident wavelength. In this case, one could suggest that the absorption behavior observed for LIA is related to a combination of light absorption and scattering by metallic Te nanocrystals.

Micro-Raman measurements with a wide-distance 50x lens were performed from two different spots of a yellowish TZN:PbS sample, as shown in Fig. 7: (i) NIA and (ii) LIA; to verify the nature of the darkening effect caused by the fs-laser during the engraving process. Fig. 7a presents the Raman spectra from NIA and LIA visualized in optical images of Fig. 7b. As observed, Raman spectrum from NIA is free of bands related to the Te–Te bonds when compared to the standard tellurium sample, while the spectrum from the brownish LIA clearly shows two bands centered at 120 cm\(^{-1}\) and 140 cm\(^{-1}\), assigned to the Te–Te bonds in the crystalline Te\(^0\) also seen on Raman spectrum of standard Te\(^0\) nanocrystals. This fact corroborates with the above results, indicating that fs-laser induces controlled localized reduction of Te\(^{4+}\) to Te\(^0\), opening opportunities for the fabrication of devices in tellurite glasses, which possess themselves great characteristics for photonic applications, such as high refractive indexes, and high solubility of rare-earth ions when compared to silica and silicate glasses.

Fig. 8a point out the Raman spectra of NIA and LIA of TZN:PbS glass sample. These two Raman spectra were recorded in two different regions on the glass surface, as highlighted in the optical microscope image (Fig. 8a).

**Fig. 8** – (a) Raman spectra of the spots on the NIA and LIA and the optical microscope image of the TZN:PbS sample (mold at 100 °C) after laser fs-laser irradiation; Raman mapping images for the bands signals intensity distribution of the Te–Te vibrational modes at (b) 119 and (c) 139 cm\(^{-1}\). The color contrast scales in the mapping images (on right-hand), ranging from black to white color, show the distribution of two \(E_u\) modes of Te\(^0\) in the TZN:PbS sample.

In contrast, there is no evidence of vibrational modes of Te\(^0\) species on NIA, indicating that tellurium stays in a fourfold oxidation state.

Fig. 8b and 8c shows the Raman mapping of bands intensities distribution for the Te–Te vibrational modes \(E_u\) at 119 and 139 cm\(^{-1}\), respectively, for a sample contain NIA and LIA. The different color contrasts observed provide information about these two specific vibrational modes within the TZN:PbS glass. From the interpretation of Raman mapping results, the Raman signal intensity distribution increases clearly for both vibrational modes of Te\(^0\) on the LIA. In detail, the color gradient varying from green to pink areas on the LIA represents the higher Raman bands intensities regions for both vibrational modes of Te\(^0\) on the LIA. Additionally, from the Raman mapping images, the individual comparison of Raman intensity distribution of bands at 119 (Fig. 8b) and 139 cm\(^{-1}\) (Fig. 8c) along the LIA shows areas with different color contrasts, which may be related to the variation of the distribution of Te\(^0\) clusters along the channels. The explanation about the formation of Te\(^0\) is based on nonlinear optical interactions promoted by femtosecond laser. Basically, the high-intensity laser beam promotes electrons from the valence to the conduction band by multiphoton absorption and photoionization processes, and these electrons can interact with ions in the glass matrix, which can result in the photoreduction reaction of Te\(^{4+}\) around the laser focal point [22]. The local heating provided by the high repetition rate of the laser enables atomic diffusion and, therefore, the aggregation of Te\(^0\) atoms to form the clusters.
photoreduction process promoted by fs-laser can be extended from dopants to glass former elements, which is relevant for glass processing technologies, mainly the ones aimed at optical devices.

4. Conclusions

In this work we demonstrate the occurrence of a redox equilibrium process involving Te⁴⁺ and S²⁻, leading to the precipitation of Te⁰ nanocrystal inside a tellurite glass depending on the cooling rate, which causes the darkening effect on the bulk samples. Te⁰ formation was demonstrated by the Raman scattering technique, enable to identify the presence of Te⁰ characteristic band, centered on 120 and 140 cm⁻¹, only in samples containing ZnS or PbS. Thus, the correlation between sulfide ions and the tellurium reduction process in the glass became evident. In the TEM images was possible to visualize particle clusters with nanometric dimensions in the matrix and the evident. In the TEM images was possible to visualize particle clusters with nanometric dimensions in the matrix and the reduction process. Aiming to control this process in localized regions, fs-laser micromachining was used and shown to be an efficient method for the local control of Te⁰ formation using a yellowish tellurite samples obtained from “slow cooling” process. The comparison of the Raman scattering spectrum of the region irradiated by the fs-laser with the non-irradiated area, shows the formation of Te⁰ in a localized channel, due to nonlinear interactions, such as multiphoton absorption and photoionization the promotes electrons from valence to conduction band and therefore photoreduction reactions. Thus, the fs-laser micromachining technique is a promising alternative able to control the reduction of tellurium in tellurite hosts, with mainly application on the production of waveguides since the formation of Te⁰ nanocrystal will change the refractive index in comparison with the glassy material around the engraving lines.

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References


