Study of absorption and IR-emission of Er\(^{3+}\), Dy\(^{3+}\), Tm\(^{3+}\) doped high-purity tellurite glasses

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Abstract. A study of high-purity TeO\(_2\)-ZnO based tellurite glasses doped with Er\(^{3+}\), Dy\(^{3+}\) or Tm\(^{3+}\) that could be used as laser media in the 2-3 μm spectral range is presented. The glasses are prepared by melting the oxides mixture inside a silica glass reactor in an atmosphere of purified oxygen. The low level of hydroxyl groups absorption allowed to measure correctly the luminescence decay characteristics of the dopants. The rare-earth ions absorption bands, the luminescence spectra and kinetic characteristics of emission from the levels \(^4\)I\(_{11/2}\), \(^4\)I\(_{13/2}\) of Er\(^{3+}\), \(^6\)H\(_{13/2}\) of Dy\(^{3+}\) and \(^3\)H\(_4\), \(^3\)H\(_5\), \(^3\)F\(_4\) of Tm\(^{3+}\) ions are investigated. The results confirm the high potential of tellurite glasses as an active media for bulk, planar waveguide and fiber lasers.

1. Introduction

Laser systems operating at 2-3 μm have important applications in both science and industry. This spectral range is characterized by a very high absorption of hydroxyl groups, so it is very attractive for surgical applications. There are several types of coherent optical sources beyond 2 μm. In recent years significant progress is demonstrated in supercontinuum generation and soliton self-frequency shift using tellurite, fluoride, germanate, and chalcogenide glass fibers [1-7]. However, the use of rare-earth ions (REI) doped fibers remains a promising way to create powerful mid-IR fiber lasers of simple design. At present, the technologies for creating continuous wave and pulsed fiber lasers operating in the range of 2-3 μm are well developed for ZBLAN fluoride glass fibers (see reviews [8-9] with references therein). Nevertheless, along with the advantages of high transparency in the mid-IR region and substantial solubility of REI, ZBLAN glass has pronounced drawbacks. It is mechanically weak, tends to crystallize and to react with atmospheric moisture.

Tellurium dioxide based glasses could be an alternative to fluoride glasses as a medium for the laser generation in the 2-3 μm range. Tellurite glasses containing oxides of tungsten, zinc, molybdenum, bismuth, alkali metals and rare-earth elements are promising materials as an active medium for the bulk, planar and fiber coherent light sources in the near and mid-IR ranges. They are characterized by a high transparency in the near and mid-IR [1], by highly nonlinear optical properties [1-3], by sufficient stability against crystallization [10, 11], and by excellent rare-earth oxides.

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solubility [12]. The transparency range of TeO₂-based glasses in the IR region is much wider than that for silicate glasses (–2.1 μm [13, 14]) and extends up to 5-6 μm for short bulk and planar devices and up to 3.5-4.5 μm for lengthy optical fibers [1, 2]. The main obstacle for their extensive applications is the difficulty to obtain the glasses with low enough concentration of 3d-transition metals impurities and OH-groups. A related problem is the lack of the adequate luminescent measurements, which can be realized only using well-dehydrated and high-purity glasses. Nevertheless the possibility to produce optical fibers with low losses up to 3-3.5 μm [15, 16] and efficient luminescence of REI up to 2.7-2.9 μm are successfully demonstrated [17-19].

One of the interesting tellurite glass compositions is the zinc-tellurite glass containing up to 30 % mol. ZnO and some modifying components such as alkali and rare-earth metals oxides. Zinc-tellurite glasses have noticeably lower phonon energy than tellurium dioxide - heavy metal oxide based systems, like tungstate-tellurite glasses. Transparency range of zinc tellurite glasses is also much wider than for tellurite glasses based on heavy metal oxides (W, Mo). The minimal level of optical losses in these glasses is estimated to be ~0.5–1 dB/m [20] and it is located in the spectral area, where silica glass optical fibers are not transparent (at ~3 μm). Like other tellurite glasses, TeO₂-ZnO based compositions are characterized by high (~2) refractive indices, sufficient chemical resistance, and significant solubility of rare-earth elements. All these properties make zinc-tellurite glasses interesting for mid-IR lasers.

Zinc-tellurite glasses doped with rare-earth ions having radiative transitions that are suitable for the mid-IR range are being actively studied at the present time. Several research groups made Er-doped TeO₂-ZnO based glasses and fibers and studied their luminescent properties, including spectroscopic parameters for the ⁴I₁₁/₂ → ⁴I₁₃/₂ energy transition near 2.7 μm [21-23].

There is a number of papers [24-26] devoted to spectroscopic analysis of Tm³⁺-doped zinc-tellurite glasses of different compositions. Despite the small branching ratio for 2.3 μm transition, the cross-section of this transition in a zinc-tellurite glass can be expected rather high due to high refractive indices and to relatively long wavelength of the transition. The estimated cross-section value is at least 3×10⁻²¹ cm² [26].

In the present investigation we have produced and studied high-purity zinc-tellurite glasses doped with Er³⁺, Dy³⁺ or Tm³⁺ because these REI have appropriate radiative transitions in the range of our interest (2-3 μm) and their absorption bands are suitable for pumping by commercially available diodes operating at 0.98-μm and at ~0.8 μm as shown in figure 1.

![Figure 1. Simplified energy levels schemes of REI.](image)

2. Glass preparation

Tellurite glasses are prepared by melting a batch in crucibles of gold or platinum inside sealed a silica chamber in purified oxygen atmosphere. Crystallization resistant zinc-tellurite glass composition modified with lanthanum and sodium oxides is chosen as a host glass matrix.

High-purity tellurium dioxide TeO₂ that is used in the synthesis is produced by the original patented method [27]. Ultrapure zinc oxide ZnO is produced by diethyl zinc oxidation. Commercially available superpurity grade lanthanum oxide La₂O₃ and sodium carbonate Na₂CO₃ are used for the glasses preparation. The total content of 3d-transition metals impurities in the mixture of initial oxides...
is determined to be 0.2–2 ppm wt and the total concentration of undesired rare-earth elements does not exceed 1–2 ppm wt same as in [28, 29].

The glass-forming melt is held at 800 °C for several hours with recurrent stirring. Then the melt is poured into silica glass moulds and annealed for several hours at a glass transition temperature. After annealing the obtained samples are extracted from the moulds and mechanically treated for further investigations. The prepared high-purity glasses are characterized by extremely low OH-group absorption less than 0.01 cm\(^{-1}\) at the peak at about 3 μm. This absorption is controlled by the procedure described in [30]. The samples with different concentrations of REI have been prepared for spectroscopic investigation.

3. Transmission spectra
The visible spectra are recorded by the spectrophotometer Lambda 900 and the IR spectra are recorded by the IR Nicolet 6700 Fourier spectrometer. The transmission spectra of glass samples doped with Er\(^{3+}\), Dy\(^{3+}\) and Tm\(^{3+}\) are shown in figure 2 a,b,c respectively. The absorption coefficients are calculated from transmission spectra by the Beer–Lambert–Bouguer equation: the volume absorption coefficient \(\alpha = \ln(1/T)/L\), where \(T\) is the transmittance; \(L\) - sample length [31].

![Transmission spectra of glass samples](image)

**Figure 2.** Transmittance spectra of the tellurite glass samples of 2-2.3 mm thick doped with different content of Er\(_2\)O\(_3\) (a), Dy\(_2\)O\(_3\) (b) or Tm\(_2\)O\(_3\) (c). Hydroxyl groups absorption in the vicinity of 3 μm is less than ~0.005 cm\(^{-1}\) in all samples.
Rare-earth doped glasses are transparent in the 0.4-5.2 μm wavelength region. The absorption bands of REI with maxima at about 1.5 μm, at both 1.7 and 2.8 μm or at 1.7 μm are observed in transmittance spectra of the tellurite glasses samples doped with different content of Er₂O₃, Dy₂O₃ or Tm₂O₃ accordingly. Thanks to the use of the original procedure of melt dehydration, the absorption bands of hydroxyl groups at around 1.5, 2.3 and 3.3 μm are not observed at the spectra of thin samples.

4. Luminescent properties of glasses
The luminescent properties of REI in the near and mid-IR ranges, including decay times under various excitation wavelengths are investigated as well. Low OH-absorption level allowed to investigate correctly the emission properties of the rare-earth dopants inside the spectral regions of hydroxyl groups absorption bands.

While excited at 0.98 μm, broad luminescence bands with maxima at ~1.5 and ~2.7 μm corresponding to electronic transitions \(^{4}I_{13/2} \rightarrow ^{4}I_{15/2}\) and \(^{4}I_{11/2} \rightarrow ^{4}I_{13/2}\) of \(\text{Er}^{3+}\) are recorded (figure 3(a)). To measure lifetimes of excited levels, we used the similar technique described in the paper [18]. This technique included short pulse excitation at the required wavelength and excludes the reabsorption.

![Figure 3](image_url)

**Figure 3.** Luminescence spectra of the tellurite glass samples of 2-2.3 mm thick doped singly with Er₂O₃ (a), Dy₂O₃ (b) and Tm₂O₃ (c) under excitation of 0.975, 0.8 and 0.8 μm, respectively.

The luminescence decay times at ~1.5 and ~0.98 μm are at the level of 3.5 ms and 250 μs, respectively, for the best samples. The results of the study showed that zinc-tellurite glasses doped with erbium ions are of considerable interest for erbium laser generation at ~2.7 μm, mostly because the upper laser lifetime in them is twice longer than in heavy metal tellurite glasses.
Luminescence band of Dy$^{3+}$ with maximum at 2.9 μm corresponding to electronic transition $^6H_{15/2} \rightarrow ^4H_{15/2}$ is registered for the Dy$_2$O$_3$ doped glass sample under 0.8 μm excitation (figure 3(b)). The lifetime of the level $^6H_{11/2}$ is equal to ~13 μs. This lifetime is determined mostly by multiphonon luminescence quenching rate.

Three emission bands of Tm$^{3+}$ with maxima at 1.46, 1.8, and 2.3 μm corresponding to electronic transitions $^3H_4 \rightarrow ^3F_4$, $^3F_4 \rightarrow ^3H_6$ and $^3H_4 \rightarrow ^3H_5$, respectively, are recorded under 0.8 μm excitation of the tellurite glass samples doped with Tm$_2$O$_3$ (figure 3(c)). The lifetimes of the $^3H_4$, $^3H_5$, $^3F_4$ levels have been determined experimentally. They are 300, 0.13 and 2660 μs, respectively for the glass with 0.1% Tm$_2$O$_3$.

5. Conclusion

We have prepared high-purity zinc-tellurite glasses doped with Er$^{3+}$, Dy$^{3+}$ or Tm$^{3+}$ and experimentally studied their absorption and luminescent properties in the near and mid-IR. Hydroxyl groups absorption in the all samples prepared is less than 0.01 cm$^{-1}$ at the maximum of the main absorption band near 3 μm. The luminescence spectra near 1.5 and 2.7 μm for Er-doped glass corresponding to $^4I_{13/2} \rightarrow ^4I_{15/2}$ and $^4I_{11/2} \rightarrow ^4I_{13/2}$ laser transitions; near 2.9 μm for Dy-doped glass corresponding to $^6H_{15/2} \rightarrow ^4F_{4}$ laser transition; and near 1.46, 1.8 and 2.3 μm for Tm-doped glass corresponding to $^3H_4 \rightarrow ^3F_4$, $^3F_4 \rightarrow ^3H_6$ and $^3H_4 \rightarrow ^3H_5$ laser transitions are recorded and analyzed. The measured lifetimes of excited levels are 3.5 ms and 250 μs for $^4I_{13/2}$ and $^4I_{11/2}$ of Er$^{3+}$; 13 μs for $^6H_{15/2}$ of Dy$^{3+}$; and 300, 0.13 and 2660 μs for $^3H_6$, $^3H_5$, and $^3F_4$ of Tm$^{3+}$, respectively. This work may provide promising active materials for lasers emitting at 1.45, 2.3 and 2.7 μm.

Acknowledgments

This work was supported by Russian Science Foundation (grant 17-12-01324).

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