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Spectroscopic investigation and optical characterization of novel highly thulium doped tellurite glasses

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ABSTRACT

In this paper, optical properties of $75TeO_2–20ZnO–5Na_2O$ host glass doped with concentration of Tm^{3+} up to 10 %mol were studied in order to assess the most suitable rare earth content for short cavity fiber lasers. Raman spectroscopy revealed a change in the glass structure while increasing Tm^{3+} content, similar to the well known addition of alkali ions in a glass. Influence of the fabrication process on the OH^- content was determined by FTIR measurements. Refractive index of Tm^{3+} doped tellurite glasses was measured at five different wavelengths ranging from 533 nm to 1533 nm. Lifetime and emission spectra measurements of the Tm^{3+} doped tellurite glasses are reported.

1. Introduction

Thulium (Tm^{3+}) is widely considered as one of the best active ions. It exhibits a wide emission spectrum, and it is able to cover a broad wavelength range, beyond the telecom window, up to 2000 nm. Fiber lasers in the 2 μm wavelength region were demonstrated in 1988 [1] and later optimized by using several pumping schemes at ~790 nm, ~1200 nm or ~1600 nm [2]. Development of a single frequency laser source around the 2 μm emission wavelength has also started to gather pace, mainly driven by a number of possible applications in the area such as remote sensing, LIDAR and medicine. In 2004, a single frequency Tm – doped silica fiber laser operating at 1735 nm with a maximum output power of 1 mW for 590 mW of launched pump power from Ti:sapphire laser was demonstrated [3] and more recently an output power of 318 mW was reached at an operating wavelength of 1935 nm using in-band pump at 1565 nm [4].

Regarding soft glasses, Tm-doped germanate glasses (0.5–10 wt% of Tm_2O_3) were studied [5] and as a result, a 4 wt% Tm_2O_3 doped 4 cm long fiber laser was fabricated. The same author [6], one year later, reported a fiber laser with the same doping concentration of 4 wt%, but 20 cm long and with a core diameter of 50 μm. Tm-doped ZB(L)AN glasses were also investigated with concentrations of Tm^{3+} ranging from 0.5 to 12 %mol [7] in order to achieve short, compact lasers.

However, to reduce the multi-phonon decay and hence to improve the performance of Tm-laser, tellurite glasses are, among oxide glasses, far better than silicate and germanate due to their phonon energies of 700 cm^{-1}, 1100 cm^{-1} and 900 cm^{-1}, respectively. Regarding literature on Tm-doped tellurite glasses, a fiber laser with lengths from 6.5 to 21 cm and 21 μm core diameter was demonstrated [8], where Tm_2O_3 concentration in the glass host ($78TeO2–12ZnO–10Na_2O$) was 0.5 wt%. Very recently, a Tm–Yb doped tellurite fiber laser was also demonstrated [9]: the fiber was 32 cm long, pumped through energy transfer to $^3H_5$ lasing level with further emitting from $^3F_4$ energy level at 1.8 μm whilst the Tm_2O_3 and Yb_2O_3 concentrations were 1 wt% and 1.5 wt%, respectively.

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The present paper concerns the investigation of various highly doped Tm-doped tellurite glasses with the aim of defining the suitable Tm doping level for the development of a compact thulium doped tellurite fiber laser. Development and optimization include better understanding of rare earth ion concentration influence on lifetime values and energy transfer dynamics. Large doping concentration increases quantum efficiency due to better overlapping of electric fields between donor and acceptor ions, but also reverse cross-relaxation will become dominant over a certain concentration value. Tellurite glasses can accept large concentration of Tm^{3+} ions and, as long as the hydroxyl level can be kept low, the effect of concentration quenching can be minimized. Efforts towards reducing the hydroxyl content during fiber processing, from glass preparation to perform fabrication, must be considered essential to improve amplifier performance [10].

Considering above publications we can conclude that the highest Tm content reported is 12 %mol, but in ZBLAN glasses, whilst in tellurite glasses the highest concentration reported is 4 %mol Tm^{3+} [11]. Thus no previous work has been up to now reported about tellurite glasses showing Tm doping up to 10 %mol and neither optimization process for short cavity (less than 10 cm in length and $\sim$50 μm of core diameter) thulium doped tellurite fiber laser has been up to now reported.

2. Experimental procedure

2.1. Glass fabrication

Glasses were prepared by melt quenching from mix powder batches, inside a glove box in a dry atmosphere with water content of about 7 ppm. The chemicals employed (together with their purity) were the following: TeO_2 (99.99%), ZnO (99+%), Na_2CO_3 (99.995%), Tm_2O_3 (99.99%). Relative molar ratio of the host glass constituent oxides was kept the same for all samples, regardless of Tm doping. The fabricated samples were based on the following notation: $(100 - x)(75TeO_2 \cdot 20ZnO \cdot 5Na_2O)$, where $x = 0.36$, 0.72, 1.08, 2.14, 3, 4, 5, 6, 7, and 10 %mol of Tm^{3+}. Glass melting was carried out in Pt crucibles at around 900 °C for 2–3 h, then pouring on a preheated brass plate at 300 °C and annealing followed. The whole process required around 20 h of operation.

2.2. Glass characterization: thermal and physical properties

Thermal analysis was performed on fabricated glasses using a Perkin–Elmer DSC-7 differential scanning calorimeter up to 550 °C under Ar flow with a heat rate of 10 °C/min in Al pans using 30 mg glass samples. Thermal analysis was employed to determine the effect of glass composition on glass stability which can be measured with the quantity $T_x - T_g$ (T_x is crystallization peak onset values and T_g is glass transition temperature). Measurements were repeated several times and the random error of ±3 °C was observed. Systematic error was deducted by calibration the instrument with indium and zinc as reference samples.

Density measurements were obtained by precise mass measurements in air and water environment on selected specimens following the Archimede's principle and using water as immersion liquid.

In order to determine resistance to plastic deformation Vickers hardness test with pyramid-shaped, diamond indenter was used. Hardness measurements were performed with 10, 15, 25, and 50 g loads in duration of 20 s. Vickers micro hardness (H_V) was calculated by suitable computer software. All the experiments were carried out at room temperature several times and errors are reported in Table 1.

The Young's modulus was determined by nondestructive impulse excitation technique (Grindo Sonic) method on a cylindrical sample having a length of 8 cm and diameter of 11 mm. Fundamental resonant frequency was excited by tapping the glass rod (ASTM E1876). Elastic modulus was then calculated by the related computer program after input of frequency, dimensions, and weight data.

2.3. Glass characterization: optical properties

Glasses were cut into 1 mm thick slices and polished to an optical quality. UV–VIS spectroscopy in transmission was carried out in order to assess the absorption spectra of the rare earth doped glasses.

Structural features of the glasses with changing Tm concentration were recorded by means of Raman spectroscopy: spectra were recorded using different instruments. The first one was Jobin Yvon T64000, triple monochromator working in subtractive mode with Coherent Innova 100 argon ion laser at wavelength 514.5 nm used for the excitation. Raman measurement offset was 1 cm^{-1}. Another instrument, FT Perkin–Elmer Spectrum GX spectrometer, was used featuring the excitation wavelength of 1064 nm. Measurements were obtained with a resolution of 4 cm^{-1} and laser power of 100 mW. FTIR spectroscopy was also carried out on the same instrument.

Refractive index was measured for all samples at five different wavelengths (533, 825, 1061, 1312 and 1533 nm) by prism coupling technique (Metricon, model 2010). The resolution of the instrument was of ±0.0001. Five scans were used for each measurement. Standard deviation in refractive index at different point of the same sample was around ±0.0003.

Lifetime measurement of Tm $^3F_4$ excited level was carried out using a laser diode pump source (Coherent S-780-3000C-200-H). Excitation power was on–off modulated with repetition frequency of 10 Hz and peak emission at 790 nm. The photodiode current was sent to a low noise amplifier (1 MHz bandwidth) the output voltage of which was therefore analyzed by an oscilloscope with bandwidth of 500 MHz (Tetronix TDS 3052). The fluorescence decay

Table 1
Tm-doped tellurite glasses prepared for the present study: Tm ion content in ppm, Tm ion concentration, glass transition (T_g), crystallization temperature (T_x), density and Vickers hardness values are reported. The experimental error for T_g and T_x is ±3 °C. T0 represents a reference sample without Tm ions.

Sample name	Tm^{3+} (ppm)	Tm^{3+} ($\times 10^{20}$ ions/cm^3)	T_g (°C)	T_x (°C)	$T_x - T_g$ (°C)	ρ (g/cm^3)	H_V (GPa)
T0	0	0	303	417	117	5.30	N.A.
T0.72	8690	1.65	310	442	132	5.32	3.0 ± 0.2
T1.08	12,993	2.47	313	447	134	5.34	N.A
T2.14	25,508	4.87	317	463	146	5.36	3.2 ± 0.3
T3	35,494	6.84	322	468	146	5.41	3.2 ± 0.2
T4	46,920	9.06	321	473	152	5.42	3.4 ± 0.2
T5	58,151	11.3	320	469	149	5.45	3.6 ± 0.1
T6	69,194	13.5	326	473	147	5.48	3.5 ± 0.1
T7	80,052	15.7	330	479	149	5.49	3.6 ± 0.1
T10	111,564	22.1	333	466	133	5.55	3.6 ± 0.1