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Novel Tm^{3+}-doped fluorotellurite glasses with enhanced quantum efficiency

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ABSTRACT

In this paper, new highly Tm^{3+}-doped tellurite glasses with host composition $75TeO_2–xZnF_2–yGeO_2–12PbO–3Nb_2O_5$ [x(5–15), y(0–5) mol%] are presented and compared to the Tm-doped tellurite glasses based on the traditional host composition: $75TeO_2–20ZnO–5Na_2O$ mol%. Enhanced quantum efficiency from $^3F_4$ level was observed for the proposed glasses and thermal stability and viscosity values make them suitable for optical fiber drawing. Besides the host composition, substantial influence of Tm^{3+} concentration on luminescence and lifetime of excited $^3F_4$ and $^3H_4$ states were discussed.

1. Introduction

Silica based glasses are widely used for optical fiber fabrication for telecommunications and high power fiber lasers, but different glass hosts are employed for more specific applications such as remote sensing, medical surgery and gas monitoring because they offer higher rare earth solubility and lower phonon energies required to allow the fabrication of short cavity lasers operating in the eye-safe, near infrared wavelength region ranging from 1.5 to 2 μm [1–3].

The choice of a glass able to host high amounts of rare earth (RE) ions plays an important role in targeting specific optical properties and performances. In the seventies, tellurite glasses were proposed for their high laser cross sections [4] and their weak self-quenching at high active ion concentration [5]. In 1994 Wang et al. [6] proposed tellurite glasses, in particular the $TeO_2–ZnO–Na_2O$ (TZN) glass system and concluded that such composition was a good candidate for fiber drawing. The main characteristics of tellurite glasses are wide transmission region (0.35–5 μm), good thermal stability, low phonon energy, and high linear and nonlinear refractive index.

In this study two different host compositions were used: (a) $75TeO_2–20ZnO–5Na_2O$ (TZN) as first proposed by Wang et al. [6] and a second one which belongs to the group of fluorotellurite glasses (b) $75TeO_2–xZnF_2–yGeO_2–12PbO–3Nb_2O_5$ (FTG). Some recent works have been carried out on the compositions similar to the last one. In particular the composition $75TeO_2–10ZnO–10PbO–5Nb_2O_5$ doped with a small concentration of Tm^{3+} targeting 1.47 μm emission for amplifier application was developed [7]. One year later, the composition $75TeO_2–10ZnO–4.5PbO–0.5PbF_2–9.4Nb_2O_5$ doped with $0.6Tm_2O_3$ was patented and a thermal stability factor of 104 °C (the difference between crystallization and glass transition temperature) achieved, but no luminescence characteristics report was attached [8]. Nazabal et al. [9] in 2003 reported $66TeO_2–10GeO_2–9ZnO–16ZnF_2$ host composition with the Er^{3+} as dopant. The most recent publication is from Liao et al. [10] in 2009 where compositions of passive glasses were $(85 - x)TeO_2–xZnF_2–12PbO–3Nb_2O_5$ (x = 0–40 mol%).

In FTG composition presented in this study tellurium oxide is a dominant component and plays the role of glass former. Chemical compounds such as zinc fluoride and germanium oxide are added in order to tune specific properties such as minimization of OH content and improvement of thermal stability, respectively.

GeO_2 plays the role of a glass former and its substitution of ZnF_2 aims at increasing refractive index and improving mechanical properties as well. Similar approach was reported for silica glasses [11].

ZnF_2 plays a similar role as ZnO due to similar ionic radius: depolymerization of the glass amorphous structure by increasing TeO_3 units. The increasing amount of ZnF_2 has a stronger effect than ZnO, but weaker than Na_2O. Each zinc ion is surrounded by six fluorine ions and each fluorine is surrounded by three zinc ions. The substitution of ZnO by ZnF_2 in the TZN host composition linearly decreases refractive index [12].

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Niobium (V) oxide increases linear and nonlinear refractive index, thermal stability, stability towards crystallization, and chemical durability [13,14]. No influence on phonon energy has been observed.

Lead (II) oxide (PbO) decreases glass stability: binary TeO_2–PbO (T_x–T_g < 50 °C) glass composition is less stable than TeO_2–Na_2O ($T_x - T_g \sim 120$ °C). It enters the glass structure as intermediate, creating Pb–O–Pb linkages and because of that changing trigonal bipyramid (tbp) and trigonal pyramid (tp) ratio [12]. In a binary composition PbO plays the role of a network modifier [15]. Decrease of T_g with increasing PbO content is also observed in germanate glasses where it was explained as a consequence of tetrahedral to octahedral coordination change of Ge atoms [16]. Thanks to its higher polarizability compared to ZnO in the TZN host, it leads to increase of refractive index [12].

This study was focused on the multi-component fluorotellurite glass family (named with the acronym "FTG") which was compared to the already well known Na_2O:ZnO:TeO_2 glass (acronym "TZN"). The main idea was to develop novel rare earth doped tellurite glass compositions with improved emission properties in the IR region with respect to state of the art tellurite glasses. For such a purpose thulium was used as an active ion with concentration up to 10.4×10^{20} cm^{-3} targeting emission at around 1.8 μm through transition from $^3F_4$ excited level to $^3H_6$ ground state. Basic glass characterization was performed in order to collect the necessary data for preparation of the fiber drawing process. The influence of host composition and Tm^{3+} concentration on the IR emission from levels $^3F_4$ and $^3H_4$ are also discussed.

The novel proposed host should be considered as the promising photonic material with possible applications for short cavity fiber lasers, infrared amplifiers and different light emitting diodes [17,18].

2. Experimental techniques

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+%), ZnO (99.99%), Na_2CO_3 (99.995%), ZnF_2 (99%), PbO (99.99%), GeO_2 (99.99%), Nb_2O_5 (99.9%), Tm_2O_3 (99.99%). Relative molar ratio of the host glass constituent oxides was kept the same for all samples, regardless of Tm^{3+} doping. The fabricated samples were based on the two host glass compositions $75TeO_2$–20ZnO–$5Na_2O$ and $75TeO_2$–$xZnF_2$–$yGeO_2$–12PbO–$3Nb_2O_5$ [x(5–15), y(0–5) mol%] doped with increasing amounts of Tm^{3+} (1, 3, 5 mol%). Glass melting was carried out in Pt crucible at around 900 °C for 4 h, then pouring on a preheated brass plate at 300 °C and annealing followed. The whole process required around 30 h of operation.

2.2. Glass characterization: thermo-mechanical 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).

Viscosity measurements are obtained by parallel-plate method (ASTM C1350M) on Perkin–Elmer TMA 7 Thermal Analysis System. Samples were cylindrical shaped with height of 4–6 and 4.5 mm in diameter. Applied static force was 100 mN with temperature gradient of 5 °C/min.

Viscosity measurements play a crucial role in determining the temperature at which the fiber drawing process occurs. It is assumed that the drawing process takes place at a temperature corresponding to a viscosity value of 10^4 Pa s ($\log(\eta) \sim 4$). Standard viscosity points which can be found in literature [19,20] are used to extrapolate the experimental data by fitting using the Vogel–Fulcher–Tammann–Hesse (VFTH) theoretical curve as the boundary conditions.

Experimental data were processed using Gent's equation [21]:

$$\eta = \frac{2 \cdot \pi \cdot F \cdot h^5}{3 \cdot V \cdot \left(\frac{dh}{dt}\right) \cdot (2 \cdot \pi \cdot h^3 + V)} \tag{1}$$

where F – applied force, $g = 9.81$ m/s^2, h – sample height, V – sample volume.

VFTH equation is used to describe non-Arrhenius behavior of glasses. It can be applied on wide temperature range with 10% accuracy [22]:

$$\log(\eta) = A + \frac{B}{T - T_0} \tag{2}$$

where $A = \log(\eta_0)$, $B = \frac{D \cdot T_0}{\ln 10}$, ($D$ is strength parameter), and T_0 is diverging temperature.

There are two characteristic points at which different kind of glasses should have similar viscosity value. First of them is the viscosity value at T_g and the other one is at high temperature, where $T_g/T \to 0$. In both cases, since different glass compositions should have similar structure complexity, the viscosity converges to the same value. Value of viscosity at T_g is widely accepted as $\sim 10^{12}$ Pa s [23]. At high temperature glass complexity of any glass composition decreases and many experimental values indicate the value of $A = -5$ [24,25] which defines second characteristic point.

Two kind of fits were made, for the fix parameter $A = -5$ and -4. Difference in calculated drawing temperature for fixed point 'A' in these two cases is ~1 °C and because of that, precise value of parameter 'A' does not play a crucial role for drawing process. Because of all these reasons and to simplify the fitting, a fixed value of $A = -5$ will be used.

2.3. Glass characterization: structural properties

Structural features of the glasses with changing Tm^{3+} concentration were recorded by means of Raman spectroscopy. The instrument used 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.

Specific glass structural order in the low frequency region, creates an excess of the vibrational density of states $g(\omega)_{\mathrm{exc}} = g(\omega) - g(\omega)_{\mathrm{Debye}}$, in comparison with Debye model which results in broad band, so called 'boson-peak' (BP) parameterized as '$g(\omega)/\omega^2$' [26]. Martin and Brenig model for reduced Raman intensity in the low frequency region is given by equation $I_R(\omega, T) = C(\omega)g(\omega)/\omega^2$ where $C(\omega)$ is a constant representing average coupling between incident light and the vibration modes of frequency ω called Raman coupling coefficient; and $g(\omega)$ is the density of vibrational states (DVS) [27]. Debye model cannot interpret $g(\omega)$, and $C(\omega)$ has no maximum as well so the interpretation of the BP stays a subject of debate. There are numerous models which propose its origin: dipolar interaction between some defects [28], involvement of soft anharmonic potentials [29], fraction-like dynamics of fractal structure [30], combination of acoustic phonons and rotational molecular modes [31].

Boson peak (BP) is temperature dependent and its position varies from 20 to 150 cm^{-1} depending on the host's composition.