



Green-to-red light tuning by up-conversion emission via energy transfer in Er^{3+} - Tm^{3+} -codoped germanium-tellurite glasses



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ABSTRACT

The luminescence properties through up-conversion emission process of Er^{3+} - Tm^{3+} -codoped germanium-tellurite glasses was carefully investigated by using UV–visible–near-infrared absorption spectroscopy, emission spectroscopy and lifetime measurement under near-infrared laser diode excitation at 976 nm. The glass samples were prepared by the conventional melt-casting technique. The Er^{3+} and Tm^{3+} ions act in this glass matrix as donor and acceptor, respectively, and can generate under 976 nm laser excitation a visible emission tunable from the green to the red color by varying the Tm^{3+} ion concentration. Two mechanisms are involved to obtain this up-conversion emission and its tunability from the green to the red light: (i) the excited state absorption (ESA) of Erbium ions Er^{3+} : ($^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$) and; (ii) the energy transfers (ETs) between Erbium Er^{3+} and Thulium Tm^{3+} ions. Such processes were studied by means of quantum efficiency and ET probability. It was verified that both of them depend on the Tm^{3+} ion concentration. The relative intensity of the red emission was increased up to 2.6 times for the glasses containing 0.1 mol% and 1.0 mol% of Thulium oxide Tm_2O_3 if compared with the Erbium Er^{3+} single doped glass. The spectroscopic study presented in this work has permitted to fully describe the color rendering, ranging from green to red through yellow and orange, of the light emitted by the Er^{3+} - Tm^{3+} -codoped germanium-tellurite glasses under a low power laser diode excitation at 976 nm (30 mW).

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1. Introduction

The conversion of infrared radiation to visible light has generated much of the current interest in upconversion processes (UC), particularly in trivalent rare-earth (RE)-ion-doped materials [1,2]. UC laser emission offers a simple and efficient alternative to the classical non-linear optical techniques as it converts infrared laser output to the visible and/or near ultraviolet light. UC materials can be used for either a visible detection of infrared radiation or displays of infrared images [3]. For example, a green UC emission under 980 nm excitation in Er^{3+} ion shows a great technological importance and draws scientific interest for exploration [4–6], e.g., the development of 2D luminescent displays that use NIR laser to generate a 2D image. In this sense, the visible UC emission in tellurite glasses can be tuned by co-doping these glasses with other RE ions via ET processes [7–9], based on resonant or non-resonant multipole–multipole interactions [10,11]. Therefore, the RE ions can act as donor/acceptor and offer the ability to integrate/tune the emission of infrared and visible lights for various applications [12, 13] and to be used in glass substrate as well for plasmonic [14,15].

Tellurite glasses doped with Er^{3+} ions have been widely studied due to their emission bandwidth in the NIR with applications for optical amplification in telecommunications window [16,17]. Such an emission band originates from the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ radiative transition centered at 1530 nm under a 980 nm laser excitation. Furthermore, Er^{3+} ions possess favorable metastable energy levels with long lifetime and relatively large absorption cross-section around 980 nm [18], resulting in a strong excited-state absorption (ESA) of top levels. Such top levels can emit light in the visible region and/or transfer the excitation energy to other RE ions [6–8]. The absorption cross-section can be even increased by codoping these glasses with Yb^{3+} ions, whose absorption cross-section at 980 nm is approximately an order of magnitude larger than that of Er^{3+} ions [19–21]. Moreover, ESA transitions and ET processes are favored by the higher nonlinear optical properties specific of tellurite glasses [22,30]. However, those mechanisms and the resulting emission intensity of visible or NIR UC depend on the tellurite glass composition [23–25]. Among the numerous tellurite-based glass systems, germanium-tellurite glasses are very good candidates for UC investigations due to their large transmittance window (visible and infrared regions), low cutoff phonon energy (about 800 cm^{-1} [30]) in comparison to oxide glasses [26,27], high refractive index, good chemical stability as well as good mechanical properties due to the addition of germanium oxide to the tellurite glass matrix. Besides, germanium-tellurite glasses show a particular combination of structural and optical

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properties [28] because they admit more than one structural unit combination [22,29,30]. These structural characteristics make this host matrix suitable for RE codoping. Er^{3+} ions can be used as sensitizers due to the above-mentioned characteristics, which make this RE an efficient convertor of infrared radiation to visible light in germanium–tellurite glasses. In this scenario, the codoping Er^{3+} (as a donor ion) and Tm^{3+} (as an acceptor ion) can yield substantial changes in the visible UC emission, since the interactions of the energy levels of both donor–acceptor ions depend on the separation distance of the ions and the ET quantum efficiency between them [23].

The present paper reports on the dependence of UC emission upon Tm^{3+} ion concentration in Er^{3+} – Tm^{3+} co-doped germanium–tellurite glasses. Under excitation at 976 nm, significant changes in the relative intensities of the green, red and NIR emissions have been observed as a function of the Tm_2O_3 nominal concentration, giving rise to a range of colors tunability, according to the CIE-1931 standards.

2. Sample preparation and experimental setup

The germanium–tellurite glass samples were prepared according to the nominal composition 74TeO_2 – 10ZnO – $10\text{Na}_2\text{O}$ – 5GeO_2 – $1\text{Er}_2\text{O}_3$ (mol%) as the host matrix. Tm_2O_3 was added at different concentrations, as shown in Table 1. The precursor powders are high purity materials (>3 N). Ten grams of precursor mixture was first dried in a platinum crucible at 450 °C and then melted at 760 °C for 1 h in an induction furnace under oxidizing conditions, maintaining a low flow of ultra-high purity oxygen within the furnace chamber. The melted glasses were then casted in a pre-heated mold, annealed at 300 °C for 2 h and slowly cooled down to room temperature so that the residual stress induced by the rapid cooling could be removed. The obtained samples of $1.0 \times 0.6 \times 0.3 \text{ cm}^3$ dimensions were finally polished up to achieve optical quality and flat parallel surfaces required for the optical characterizations.

The thermal properties of the glass samples were studied by differential scanning calorimetry (Netzsch DSC 404F3) in Al pans at a heating rate of 10 °C/min. Their density was measured by the Archimedes method using an MD-300S electronic densimeter (Alfa Mirage) and distilled water as the immersion liquid. The absorption spectra, which ranged from 300 to 1050 nm, were recorded on a Varian Cary 500Scan UV–Vis–NIR double beam spectrophotometer of $\pm 0.5 \text{ nm}$ resolution. Steady-state luminescence spectra were obtained by a Horiba Jobin Yvon Nanolog spectrofluorometer equipped with an R928 photomultiplier tube (PMT) multi-alkali PMT ambient-cooled visible detector. The measurements were performed over the 480 to 850 nm wavelength range by maintaining the same conditions for all samples. A laser diode operating at 976 nm coupled with a standard monomode pigtailed fiber (SMF28) was used as an external excitation source. After collimation, the laser excitation beam was focused on the sample surface through a 50 mm lens, giving a beam spot diameter of about 1 mm. The method of measurement chosen here was the ‘front face detection mode’ where emission is collected at an angle of 30° relative to the excitation beam in order to minimize re-absorption and stray light reflection. For the measurements of the Er^{3+} : $^4\text{S}_{3/2}$ and Er^{3+} : $^4\text{F}_{9/2}$

excited states lifetime, the samples were excited with a Pico-Quant pulsed laser diode at 976 nm (model LDH-P-C) with 60 ps pulse train and 50 μs dead time by using the same excitation and detection configuration as described above. The pulsed laser beam was also focused on the sample surface through the same 50 mm lens. The time resolved emission signals centered at 547 ± 2 and $652 \pm 2 \text{ nm}$ were measured by a PMT R928 module detector coupled to the Nanolog system using a Time Correlated Single-Photon Counting (TCSPC) method. All measurements were carried out at room temperature.

3. Results and discussions

The glass transition temperature of the Tm-free germanium–tellurite glass was determined at $T_g = 318 \pm 2 \text{ °C}$, while its onset crystallization temperature is $T_x = 491 \pm 1 \text{ °C}$. From the glass density we can calculate the Tm^{3+} ion concentrations as well as the distance between the Er^{3+} and Tm^{3+} ions (inter-ionic distance r_m [31–33]) in the glasses, Table 1.

Fig. 1 shows the absorption spectra of the glass samples with the corresponding transitions of the REs from the ground state to the different excited states. The Er^{3+} transition from the ground state to the $^4\text{I}_{11/2}$ state shows no change for the samples, since the Er_2O_3 nominal concentration is kept constant (1.0 mol%). Thus, it exhibits constant oscillator strength and absorption band of $\Delta\lambda \approx 15 \text{ nm}$, required for the application, i.e. the effects of the ET from the sensitizer depend only on the Tm^{3+} ion concentration. The absorption spectra revealed that the relative intensities of absorption peaks of Tm^{3+} ion increase with the increment in the Tm_2O_3 nominal concentration.

Fig. 2(a) shows the UC emission spectra of Er^{3+} / Tm^{3+} -co-doped samples as a function of Tm_2O_3 concentration pumped with a diode laser at 976 nm and 30 mW power. In this case, the emissions centered at 527, 547, 657 and 794 nm originate from the four transitions $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$, and $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{15/2}$, characteristic of the Er^{3+} ions. The relative intensity of the UC green emissions at 527 and 547 nm decreases by increasing the Tm_2O_3 concentration. In comparison to the Tm-free glass sample, the intensity of this emission decreases approximately 1.6 to 6.7 times from the Tm100 sample to the Tm1.0 sample, respectively. On the other hand, the UC intensity of the red emission at 651 nm increases approximately 2.6 times for the same Tm100 and Tm1.0 samples. These changes in the relative intensities are due to the energy transfers ET_1 (Er^{3+} : $(^2\text{H}_{11/2}, ^4\text{S}_{3/2}) \rightarrow \text{Tm}^{3+}$: $(^2\text{F}_{2,3})$) and ET_2 (Er^{3+} : $(^4\text{F}_{9/2}) \rightarrow \text{Tm}^{3+}$: $(^2\text{F}_{2,3})$), as depicted in the simplified energy diagram presented in Fig. 3(a) which summarizes the involved excitation mechanisms and relaxation pathways for the Er^{3+} and Tm^{3+} ions. It is worth noting from Fig. 3(a) that due to the large energy difference between the Er^{3+} : $(^2\text{H}_{11/2}, ^4\text{S}_{3/2})$ and Tm^{3+} : $(^2\text{F}_{2,3})$ levels if compared to that between the Er^{3+} : $(^4\text{S}_{3/2})$ and Er^{3+} : $(^4\text{F}_{9/2})$ levels where non-radiative transition may occur, the ET_1 process is expected to be dominant over the ET_2 one for the red emission at 651 nm. A significant decrease in the red UC is observed for higher Tm_2O_3 concentrations, which can be associated with concentration quenching effects [34]. This quenching is ascribed to the cross-relaxation between two nearby Tm^{3+} ions (higher Tm^{3+} ion concentration and shorter distance separation, as

Table 1

Physical properties of the germanium–tellurite glasses as a function of Tm_2O_3 nominal concentration with respective sample labeling used in the text.

Glass label	Tm_2O_3 (mol%)	$N_{\text{Er}^{3+}} \pm 0.08 \times 10^{20} \text{ ions/cm}^3$	$N_{\text{Tm}^{3+}} \pm 0.08 \times 10^x \text{ ions/cm}^3$	$\rho \pm 0.07 \text{ g/cm}^3$	$r_m = \{r_d, r_a, r_{d-a}\}^b$
Tm000 ^a	0.000	7.82	–	4.95	
Tm025	0.025	8.11	2.04×10^{19}	5.22	
Tm050	0.050	8.12	4.09×10^{19}	5.21	
Tm100	0.100	8.22	8.29×10^{19}	5.22	{23.0, 49.4, 23.8}
Tm1.0	1.00	8.03	8.11×10^{20}	5.23	{23.2, 23.1, 113.2}
Tm1.5	1.50	8.03	1.22×10^{21}	5.28	
Tm2.0	2.00	8.00	1.56×10^{21}	5.25	

^a Host matrix (Er^{3+} single doped glass).

^b r_d , r_a and r_{d-a} are the distances between donor, acceptor and donor–acceptor ions, respectively in Angstroms (Å).

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