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Optical spectroscopy of TeO_2–GeO_2 glasses activated with Er^{3+} and Tm^{3+} ions

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Abstract

The optical and spectroscopic properties of Er^{3+}- and Tm^{3+}-activated germano-tellurite glasses of molar composition $90TeO_2$:$10GeO_2$ and $80GeO_2$:$20TeO_2$, prepared by melt-quenching, have been studied. The refractive indices at three different wavelengths in the visible and near infrared have been measured. The vibrational properties of the glasses were studied by Raman spectroscopy. The Raman spectra indicate that the GeO_2 and TeO_2 components of the glasses do not mix well at the microscopic level. The spectroscopic properties of the rare earth ions were investigated by absorption spectroscopy and time resolved photoluminescence. The Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition shows a bandwidth of about 70 nm with a lifetime of about 3 ms. The $^3H_4 \rightarrow {}^3F_4$ transition of Tm^{3+} ion has a bandwidth of 115 nm in the TeO_2-based glass, and of 135 nm in the GeO_2-based glass. The lifetime of $^3H_4$ is less than 0.2 ms.

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1. Introduction

The demand for transmission capacity is matched by the recent availability of optical fibers with low loss between 1280 and 1700 nm for wavelength division multiplexing (WDM) [1]. The choice of a suitable host glass matrix for rare earth (RE) ion dopants is a key factor in designing optical amplifier for this broad region, as quantum efficiency and emission bandwidth depend strongly on the structural properties of the host glass [1].

In this respect, tellurite glasses have many advantages such as solubility for RE ions, a transmission region 0.35–6 μm, phonon energies <800 cm^{-1} and glass stability [2]. GeO_2-based glasses have lower T_g and phonon energy than SiO_2 based glasses, and transparency in the near infrared region [3].

Tellurite glasses have been shown [2,4,5] to be candidates as Er^{3+} hosts to substitute or complement the silica-based glasses, as they combine a $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission bandwidth as broad as 60 nm, extended to 1630 nm, with acceptable properties for fiber drawing and planar waveguide fabrication. Moreover, the use of thulium ions will make possible a band extension in the spectral range from 1450 to 1500 nm, the S-band amplifier region [6–8].

In this work, Er^{3+}- and Tm^{3+}-activated germano-tellurite glasses of molar composition $90TeO_2$:$10GeO_2$ and $80GeO_2$:$20TeO_2$, prepared by melt-quenching, have been studied.

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2. Experimental

Glasses of nominal compositions $90TeO_2{:}10GeO_2$ (hereafter called TG) and $80GeO_2{:}20TeO_2$ (hereafter called GT) doped with Er^{3+} (TGEr; GTEr) or Tm^{3+} (TGTm; GTTm) were prepared from 99.99% grade oxides (Aldrich) as reported in Table 1.

Powders of TeO_2, GeO_2, and Er_2O_3 or Tm_2O_3 were mixed and melted in platinum crucibles at 800 °C (TG) and 1100 °C (GT) in air for 30 min. Glass was obtained by quenching the bottom of the crucible in a freezing mixture of ice and water. The TeO_2 and GeO_2 based glasses were then annealed for 30 min at a few degrees below the glass transition temperature (325 °C and at 450 °C, respectively).

The refractive index of the glasses was measured by the prism-coupling method, using a rutile prism. Optical absorption spectra were obtained in the visible and near infrared regions (0.4–3.2 μm) using a double beam spectrometer with a resolution of 0.5 nm.

The VV polarized Raman spectra were obtained by exciting the samples with the 458 nm and the 514.5 nm emission lines of an Ar^+-ion laser, for the glasses doped with Er^{3+} and Tm^{3+}, respectively, to avoid a superposition between Raman and luminescence signals. The scattered radiation was selected by a double monochromator with a resolution of 2 cm^{-1} and analyzed by a photon-counting system.

Photoluminescence (PL) spectroscopy, in the region of the transitions $^4I_{13/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ion and $^3H_4 \rightarrow {}^3F_4$ of Tm^{3+} ion [8] was performed using the 514.5 nm and 476 nm lines of an Ar^+-ion laser, respectively, as excitation source. The luminescence was dispersed by a 320 mm single-grating monochromator with a resolution of 2 nm. The light was detected using an InGaAs photodiode and a lock-in technique. Decay curves of $^4I_{13/2}$ erbium metastable level were obtained by chopping the CW exciting beam with a mechanical chopper and recording the signal at 1534 nm with a digital oscilloscope. The lifetime of $^3H_4$ thulium level was evaluated collecting the $^3H_4 \rightarrow {}^3H_6$ luminescence at 800 nm. The excitation was at 355 nm by the third harmonic of a Q-switched Nd^{3+}:YAG laser, with a pulse width of 6 ns and a repetition rate of 10 Hz. The signal was detected by a photon counting unit connected to a multichannel digital analyzer. All the measurements were performed at room temperature.

Table 1
Nominal composition and labelling of the samples

Label	Molar composition			
	TeO_2	GeO_2	Er_2O_3	Tm_2O_3
TGEr	89.55	9.95	0.50	–
TGTm	89.55	9.95	–	0.50
GTEr	19.95	79.80	0.25	–
GTTm	19.95	79.80	–	0.25

3. Results

Table 2 reports the refractive indices of the GeO_2 and TeO_2 based glasses measured at three wavelengths in the visible and infrared region. The measured refractive indices are in agreement to within 0.01 with those calculated using the Lorentz–Lorenz equation [9] and nominal composition.

Fig. 1 shows the absorption spectra of the four samples in the range between 0.4 μm and 3.2 μm. The bands, assigned to the electronic transitions from the rare earth ground state ($^4I_{15/2}$ level for the erbium doped glasses (Fig. 1(a)) and $^3H_6$ for the thulium doped glasses (Fig. 1(b))), are labelled by the excited states $^{2S+1}L_J$ [7,10]. The band peaked at around 2.8 μm, in the GT samples, and the broader band at about 3 μm, in the TG samples

Table 2
Refractive index (±0.001), lifetime (±10%) of the $^4I_{13/2}$ state (for Er^{3+}) and of the $^3H_4$ (for Tm^{3+}) and full width at half maximum (FWHM, ±4 nm) of the luminescence bands ($^4I_{13/2} \rightarrow {}^4I_{15/2}$ for Er^{3+}; $^3H_4 \rightarrow {}^3F_4$ for Tm^{3+}) for the TG ($90TeO_2{:}10GeO_2$) and GT ($80GeO_2{:}20TeO_2$) glasses

Sample	TGEr	TGTm	GTEr	GTTm
n @ 632 nm	2.123	2.110	1.691	1.700
n @ 543 nm	2.148	2.140	1.708	1.710
n @ 1542 nm	2.061	–	1.642	–
Lifetime (ms)	3.4	0.15	1.0 and 3.6	0.02 and 0.15
FWHM (nm)	68	115	69	135

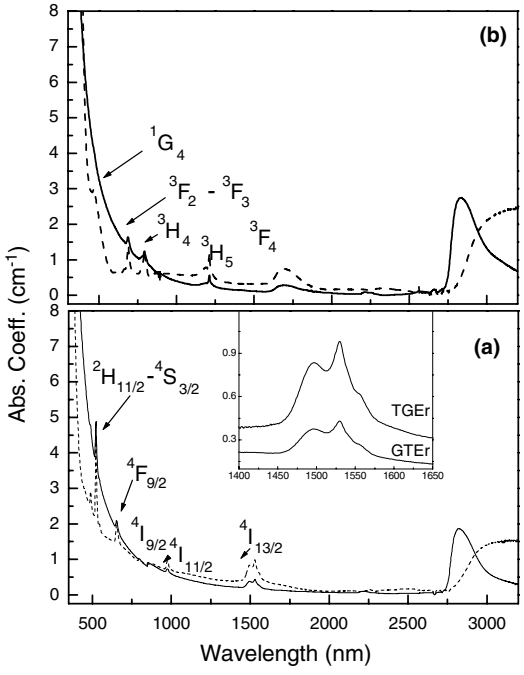

Fig. 1. Absorption spectra of GTEr (solid line) and TGEr (dashed line) (a) of GTTm (solid line) and TGTm (dashed line) (b). The inset shows, magnified, the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition of erbium ions.