Journal of Luminescence 129 (2009) 270–276

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Spectral broadening and luminescence quenching of 1.53 μm emission in Er^{3+}-doped zinc tellurite glass

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ARTICLE INFO

Article history:
Received 30 January 2008
Received in revised form
9 August 2008
Accepted 13 October 2008
Available online 29 October 2008

Keywords:
Tellurite glass
Erbium: Er^{3+}
Reabsorption
Hydroxyl groups

ABSTRACT

The emission spectra and the lifetime of the lasing transition $^4I_{13/2}\rightarrow{}^4I_{15/2}$ in Er^{3+}-doped TeO_2-ZnO binary glass have been studied. The investigation includes Raman scattering spectroscopy as well as optical absorption, luminescence, and lifetime measurements techniques. The influence of erbium concentration on the line-shape of this electron transition has been analyzed. It was observed that the increasing of Er^{3+} ion concentration, in the 0.2–4 mol% range, results in a structural changes and a significant spectral broadening of the 1.53 μm emission band. Reabsorption has been evoked to explain the broadening of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ emission line. In the paper, is also reported the effect of the erbium content on the emission intensity of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition as well as on the lifetime of the $^4I_{13/2}$ level. Based on the electrical–dipole interaction theory, the luminescence concentration quenching mechanism by hydroxyl groups is analyzed. The data suggest that $<10\%$ of hydroxyl groups are coupled to erbium ions in the zinc tellurite glass network.

1. Introduction

Due to the increasing demand for information capacity of wavelength division multiplexing (WDM) networks, it is desirable that the erbium-doped fiber amplifier (EDFA) has a broad and flat gain spectrum within the telecommunication window [1,2]. So far, many researchers have paid much attention to silicate [3], germanate [4], phosphate [5], fluoride [6], bismuth [7,8], and tellurite glasses [9], probably better suited for fiber amplifiers.

Although the silica-based erbium-doped fiber has a good thermal stability, high chemical durability, and most importantly the mechanical stability, the silica-based EDFA still has some disadvantages especially on the narrow gain spectrum which only permits fewer channels to limit its application. However, tellurite-based EDFA was reported to have 80 nm wide and flat gains up to 1.5 μm, which also shows various excellent material properties such as lowest phonon energy ($\sim$750 cm^{-1}) among oxide glasses, high refractive index ($\sim$2), high dielectric constants, strength and corrosion resistance over fluoride glass and rare-earth (RE) ion solubility [10–13]. Numerous special optical properties i.e., large emission cross-section and broad fluorescence full-width at half-maximum identify Er^{3+}-doped tellurite glasses as attractive materials for potential applications in high-performance fiber amplifiers, as well as optics and laser technology.

Recently, as a result of the development of optical network systems [14], there have been intensive studies on compact amplifiers such as short-length fiber amplifier or Er-doped planar waveguide amplifiers [15–19]. For the amplifiers with the short effective length, it is necessary that the doping concentration of Er^{3+} ions in the devices is sufficiently high. At higher Er^{3+} concentrations, however, the luminescence shows a quenching by energy transfer processes, due to interactions between Er^{3+} ions and hydroxyl (OH^-) groups [20,21], and in addition, another cooperative upconversion process occurs if a high pump power is applied as well [22].

Several works on Er^{3+}-doped tellurite glasses have been reported by authors in the last decade [23–30]. There, mainly the effect of Er^{3+} concentration on the spectroscopic properties has been studied. However, up to now there is only a few experimental works on the effect of erbium content on structural properties [31–33] and on spectral broadening [34,35] have been reported. At the same time, many research works have been carried out to study the quenching effect of OH^- groups on the $^4I_{13/2}$ level of Er^{3+} in silicate, borosilicate and phosphate glasses [20,21]. Nevertheless, little is known about the OH^- quenching on emission properties in different Er concentrations of Er^{3+}-doped tellurite glasses. Thus, it is very necessary to reveal the effects of high erbium doping levels on the local field of erbium sites, the spectral broadening at 1.53 μm and concentration quenching. Such investigations should provide great progress in the engineering of EDFA.

This paper reports on the effects of the Er_2O_3 content on the local structure and on spectroscopic properties of Er^{3+}-doped

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doi:10.1016/j.jlumin.2008.10.006

tellurite zinc (TZ) glass system as well. The doping concentration ranges from 0.2 to 4 mol% Er_2O_3. Especially, the effect on the spectral broadening of the 1.53 μm emission is analyzed and discussed. The analysis of OH^- and Er^{3+} concentration quenching in erbium-doped TZ glass has been also carried out. Glasses were investigated using Raman spectroscopy, optical absorption, photoluminescence (PL), and time-resolved luminescence measurements at room temperature (RT).

2. Experimental

Glasses were prepared from oxide powders of TeO_2, ZnO, and Er_2O_3 as starting materials using the conventional melt-quenching method. Batches of 10 g were melted in platinum crucibles at 900 °C in an electrically heated furnace in the air atmosphere. In order to investigate the effect of OH^- groups on concentration quenching, no removing OH^- process by bubbling oxygen was adopted in melting glass. The amount of dopant was varied between 0.2 and 4 mol% Er_2O_3. The visible (vis) and near-infrared (NIR) absorption spectra were measured using a Perkin-Elmer UV/vis/NIR Lambda 900 spectrophotometer in the 400–1700 nm range. IR transmission spectra were measured using a Perkin-Elmer GX II FTIR spectrophotometer. PL spectra were recorded by exciting the samples with a cw near-infrared Ti:saphire laser tuned to 797 nm pumped with an Ar^+ ion laser Spectra-Physics 2017. The emitted light was dispersed by a Jobin–Yvon HRD1 monochromator and detected with a Hamamatsu HV 1250 photomultiplier. The signal from the detector was preamplified and passed to a lock-in amplifier whose reference was a variable speed light chopper in the excitation beam. The experimental lifetimes of the levels were obtained by exciting the samples with a laser analytical systems dye laser, tuned to 980 nm, pumped by a pulsed frequency doubled Nd:YAG laser from IBM Industries. The duration of pulses was 8 ns. The emitted light has been focused on a Jobin–Yvon HR S2 spectrophotometer. The detection has been performed using an R 1767 Hamamatsu photomultiplier and a Lecroy 9410 averager oscilloscope. Raman measurements were performed using a double grating spectrometer (XY Dilor) with the 457.9 nm Ar^+ ion laser exciting line. All Raman spectra were recorded, in the wavenumber range 300–1000 cm^{-1} under a vertical–vertical (VV) polarization, with a spectral slit width of 0.6 cm^{-1}. All measurements were recorded at RT.

3. Results and discussion

3.1. Raman analysis

In order to investigate the evolution of the glass structure with the adding of Er_2O_3, Raman measurements were carried out on undoped and Er^{3+}-doped TZ glass samples. Fig. 1 shows VV Raman spectra of the base line TZ glass and the 4 mol% Er^{3+}-doped glass, both have been measured under 457.9 nm excitation line. In the wave-numbers range 300–1000 cm^{-1}, each spectrum exhibits two bands centred around 675 and 750 cm^{-1} and a third smaller amplitude band located at 450 cm^{-1}. The band at 675 cm^{-1} is assigned to the stretching vibrations of the TeO_4 trigonal bypiramidal (*tbp*) groups. They are linked through Te–O–Te, with O in a position alternatively axial and equatorial, and form the backbone of pure TeO_2-based crystals or glasses [36]. While the band at 750 cm^{-1} arises from TeO_3 and TeO_{3+1} vibration [37,38]. To determine the ratio of the Raman signal of the 750 cm^{-1} Raman band for doped samples to that in the undoped glass, we have normalized Raman spectra relative to the maximum intensity of the band at 675 cm^{-1}. As shown, the adding of erbium oxide results in a growing of the peak around 750 cm^{-1} (inset of Fig. 1) with a slight blue shift with the increasing Er^{3+} ion concentration. Controversly, the intensity of the Raman band near 450 cm^{-1} decreases with increased Er_2O_3 content. A shift towards smaller wave-numbers has been observed for the peak frequency of the band. It should be noticed that the presence of erbium, even in relatively high doping levels, does not lead to the development of structural peaks, indicating a very good dispersion of RE ions, with no evidence of the formation of clusters [36].

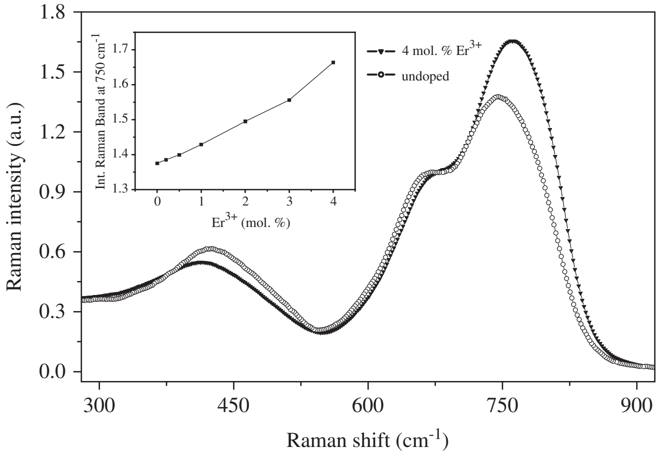

Fig. 1. RT Raman spectra of the TZ glass : (○) undoped glass and (▲) 4 mol% Er_2O_3-doped glass. The inset shows the intensity of 750 cm^{-1} Raman band versus erbium ion concentration.

The progressive enhancement of the Raman peak intensity at 750 cm^{-1} can be explained as due to the evolution of TeO_{3+1} and TeO_3 structures with the increasing erbium concentration. The results show that the erbium ion acts as a lattice modifier in the binary tellurite glasses, i.e., it converts TeO_4 *tbp* units to primarily TeO_3 trigonal pyramids units, and possibly some terminal TeO_{3+1} polyhedra [39]. The significant change of the 450 cm^{-1} Raman band, associated with the Te–O–Te linkages, is attributed to a structure disruption of the tellurite network and to a decrease in the Te coordination number as the erbium content increases [40]. Initially, TZ glass contains a variety of structural motives (TeO_4, TeO_3, and TeO_{3+1}) due to the presence of Zn^{2+} modifier ions, which give rise to a large distribution of structural sites. Adding erbium ions further enhances the variety of the network-forming TeO_x species, resulting in the enhancement of structural disorder. As a consequence, the addition of erbium ions in the tellurite glass system induces a diversity of dopant sites and then may gives rise to a broadening of the emission lines. In this context, Jha et al. [35] suggest that with the increasing dopant concentrations in a tellurite glass network, the Stark sublevel splitting increases, thereby indicating that the Er^{3+} ions occupy new sites at higher concentrations, which leads to a further line-shape modification [35]. The variations in the Er^{3+} local environment, symmetry, and ligand field strength may induce spectral broadening of the Er^{3+} emission.

3.2. Emission spectra and cross-section at 1.5 μm

Raman analysis demonstrates that, with increasing erbium content in the glass network, some structural changes take place. A spectroscopic study is indeed required to investigate the importance of these changes and their possible role on optical properties. Fig. 2 shows RT luminescence spectra in the wavelength range 1450–1700 nm obtained on the lightly (0.2 mol%) and heavily (4 mol%) doped TZ glass pumped with 797 nm excitation line. The figure also shows the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ absorption band of an