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The origin of spectral broadening of 1.53 μm emission in Er^{3+}-doped zinc tellurite glass

N. Jaba [a,*], H.B. Mansour [a], B. Champagnon [b]

[a] Laboratoire de Physique des Semi-conducteurs, Département de Physique, Faculté des Sciences, 5019 Monastir, Tunisia

[b] Laboratoire de Physico-chimie des Matériaux Luminescents, UMR 5620 CNRS, Université Claude Bernard Lyon 1, Bât. A. Kastler, 10 rue Ampère, 69622 Villeurbanne Cedex, France

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ABSTRACT

The emission spectra of the lasing transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ in Er^{3+}-doped TeO_2–ZnO binary glass have been studied. The influence of the concentration of Er_2O_3 and sample-thickness on the line-shape of this electron transition has been analyzed. The investigation includes Raman scattering spectroscopy as well as optical absorption and photoluminescence. 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 as a main mechanism to explain the broadening of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission line.

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 particularly their optimal refractive index matched with fiber networks, the silica-based EDFA still exists some disadvantages especially on the narrow gain spectrum which only permits fewer channels 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 dielectric constants, and 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.

Most tellurite glass systems require at least 50 mol% TeO_2 for glass formation. The broad range of glass forming compositions provides a variety of structural motives for the network-forming TeO_x species. Such species include bipyramidal TeO_4 groups at high TeO_2 content and isolated pyramidal TeO_3 groups at low TeO_2 content [14]. This assortment of species should provide a significant variety of structural sites for the incorporation of dopant species, such as erbium ions and then give rise to a broadened emission spectrum [15].

Recently, several works on Er^{3+}-doped tellurite glasses have been reported by authors. There, mainly the effect of Er^{3+} concentration on the spectroscopic properties has been studied [16–23]. However, only a few experimental works on the effect of erbium content on structural properties [24–26] and on spectral broadening [27,28] have been reported. Thus, it is very necessary to reveal the effect of high erbium doping levels on the local field of erbium sites and the spectral broadening at 1.53 μm. Such investigations should provide great progress in the engineering of EDFA.

In this article, we investigate the effects of the Er_2O_3 content on the local structure and on spectroscopic properties of Er^{3+}-doped tellurite zinc (TZ) glasses. The doping concentration ranges from 0.2 to 4 mol% Er_2O_3. Especially, the effect on the spectral broadening of the 1.5 μm emission is analyzed and discussed. Glasses were investigated by means of Raman spectroscopy, visible and near-infrared absorption and luminescence measurements at room temperature (RT). The Judd–Ofelt (J–O) intensity parameters have been calculated using the absorption spectra and J–O theory in order to

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* Corresponding author.
E-mail addresses: nejeh.jaba@yahoo.fr, nejeh.jaba@fsm.rnu.tn (N. Jaba).

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evaluate the stimulated emission cross-section of the lasing transition $^4I_{13/2}\rightarrow{}^4I_{15/2}$.

2. Experimental

A series of glasses with the nominal molar composition $70TeO_2-30ZnO-xEr_2O_3$ where $x = 0.2, 0.5, 1, 2, 3, 4$ were prepared 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. The amount of dopant was varied between 0.2 and 4 mol% Er_2O_3. 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}. The visible (vis) and near-infrared (NIR) absorption spectra were measured at RT using a Perkin–Elmer UV/vis/NIR Lambda 900 spectrophotometer in the 400–1700 nm range. Photoluminescence (PL) spectra were recorded by exciting the samples with a CW NIR 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. 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 [14]. While the band at 750 cm^{-1} arises from TeO_3 and TeO_{3+1} vibration [29,30]. 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 [14].

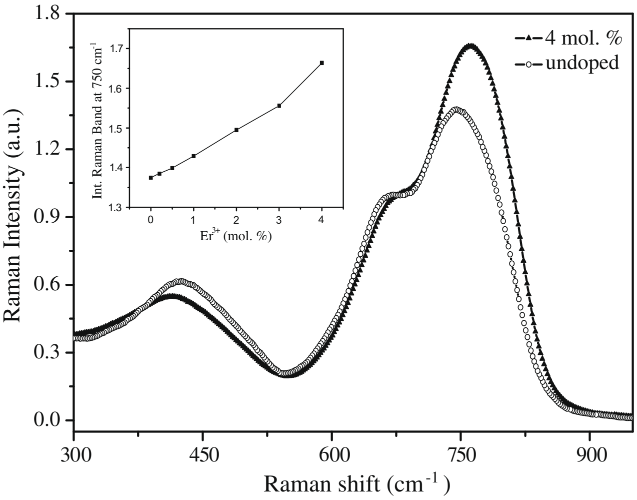

Fig. 1. Room temperature Raman spectra of the TZ glass: (o) non-doped glass and (▲) 4 mol% Er_2O_3-doped glass. The inset shows the intensity of 750 cm^{-1} Raman band as a function of erbium ion concentration.

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 [31]. 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 [32]. 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. [28] 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 [28]. The variations in the Er^{3+} local environment, symmetry, and ligand field strength may induce spectral broadening of the Er^{3+} emission.

3.2. Absorption spectra and Judd–Ofelt analysis

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 typical absorption spectrum of the glass samples. Each assignment corresponds to the excited level of Er^{3+}. No significant change is observed for the line-shape and/or for the bandwidth of absorption bands as erbium content is increased.

Absorption cross-section of ground-state absorption is given by

$$\sigma_a(\lambda) = \frac{2.303\,log(I_0/I)}{NL} \quad (1)$$

where $log(I_0/I)$ is the absorbance, L is the thickness of the glass samples in cm, and N represents the RE concentration per cm^3 in the glass. The absorption cross-section of Er^{3+}: $^4I_{15/2}\rightarrow{}^4I_{13/2}$ for the TZ glass at peak value is 8.16×10^{-21} cm^2.

The J–O theory [33,34] is a useful tool for analyzing the spectral property of RE ions doped glasses. The three parameters $\Omega_t(t = 2, 4, 6)$ were determined from the experimentally measured absorption spectra by a least-square fitting approach. Accordingly, six absorption bands ($^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, and $^4I_{11/2}$), which are related to the electric-dipole transitions, have been chosen to do the fitting. The $^4I_{13/2}$ level is, however, excluded because of the contribution of magnetic-dipole transition. The intensity parameters