



# Enhancement of spectroscopic and luminescence properties of $\text{Er}^{3+}$ doped tellurite glasses by adding $\text{P}_2\text{O}_5$ for lasing materials



I. Jlassi<sup>a,b,\*</sup>, H. Fares<sup>c</sup>, H. Elhouichet<sup>a,b</sup>

<sup>a</sup> Laboratoire de Physico-Chimie des Matériaux Minéraux et leurs Applications, Centre National de Recherches en Sciences des Matériaux, B.P.95, Hammam-Lif 2050, Tunisia

<sup>b</sup> Département de Physique, Faculté des Sciences de Tunis, Université de Tunis El Manar, Campus Universitaire Farhat Hachad, ElManar 2092, Tunisia

<sup>c</sup> Institute of Chemistry - São Paulo State University - Unesp, P. O. Box 355, Araraquara, SP 14801-970, Brazil

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## ABSTRACT

$\text{Er}^{3+}$ -doped phosphor-tellurite glasses has been synthesized by conventional melting method. Results of differential scanning calorimetry (DSC) measurements indicate a good thermal stability of tellurite glasses. The DSC measurements show an improvement of thermal stability of glass hosts after adding  $\text{P}_2\text{O}_5$ . The structures of glasses were investigated by X-ray diffraction (XRD) and Raman spectroscopy to understand their dependence of structure on composition. Absorption spectrum from near infrared to visible was obtained and the Judd–Ofelt (J–O) intensity parameters ( $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$ ) were determined. Spontaneous emission probabilities of some relevant transitions, branching ratio, and radiative lifetimes of several excited states of  $\text{Er}^{3+}$  have been predicted using intensity J–O parameters. Up-conversion luminescence characteristics, under 977 nm excitation wavelength, have been investigated at room and low temperature in these glasses. Intense green and red emissions from  $\text{Er}^{3+}$  centered at 534 nm, 548 nm and 660 nm, corresponding to the transitions  ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ ,  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  and  ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ , respectively, were simultaneously observed. The quadratic dependence of the up-conversion emission on the excitation power indicates that two-photon steps are involved for the three visible emission bands. The PL lifetimes is found to decrease in the temperature range 77–300 K. Using the Mc-Cumber method, emission cross-section ( $\sigma_e$ ), Absorption cross-section ( $\sigma_a$ ), and gain cross-section ( $G(\lambda)$ ) for the  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  transition, were calculated. By analyzing obtained data based to all advantages after adding  $\text{P}_2\text{O}_5$ , the tellurite glasses can be used as potential host material for developing optical amplifiers applied for 1.53  $\mu\text{m}$  band broad and high-gain erbium-doped fiber amplifiers (EDFA).

## 1. Introduction

Study of spectroscopic properties of rare earth (RE) ions in crystalline/amorphous materials has been carried out by many researchers for the past few decades due to its potential applications in many fields [1]. Among the trivalent rare earth ions,  $\text{Er}^{3+}$  ion is one of the most suitable rare earth ions for up-conversion processes due to its favorable energy level structure [2]. Tellurium oxide based glasses attracted the scientific community due to their application in the field of glass ceramics, optical amplifiers and non-linear optical devices [3]. These glasses have low phonon energy [4], low glass transition temperature, low crystallization ability [5], good chemical resistance [6], good transmission for infrared rays with a wide range of wavelength [7] and large refractive indices [8] such as bio medical lasers, underwater and satellite communication, optical data storage and bar code reading etc. Among lanthanides,  $\text{Er}^{3+}$  ion possesses peculiar applications in a

variety of fields such as eye safe lasers (1.53  $\mu\text{m}$ ), frequency up converter, photo chromic applications, telecommunication field, display devices and energy transfer studies [9].

In order to meet the required applications of RE ions, optimization of host matrix is more important. Nowadays selection of two glass formers is more common due to its practical interest in scientific technology where the structural network is greatly perturbed. Tellurite glasses possess excellent properties like transparency, refractive index, low phonon energy (850  $\text{cm}^{-1}$ ), good corrosion resistance over fluoride glasses and high RE ion solubility [10]. In addition, these glasses help one to improve the emission cross-section and band width for EDFA. Similarly with quite high phonon energy, phosphate is introduced into the network to reduce the up-conversion phenomena and to increase the band width for eye safe laser. With the introduction of phosphate into the network, a structural change takes place due to the peculiar nature of phosphate which has the ability to exist in two coordination

\* Corresponding author at: Département de Physique, Faculté des Sciences de Tunis, Université de Tunis El Manar, Campus Universitaire Farhat Hachad, ElManar 2092, Tunisia.  
E-mail address: [ifa.jlassi@gmail.com](mailto:ifa.jlassi@gmail.com) (I. Jlassi).

states such as trigonal and tetragonal states. Introducing phosphate into  $\text{Er}^{3+}$ -doped tellurite glasses enhances the solubility of rare earth ions. Lots of researches [11–13] have been performed on the optical and thermal properties of tellurite–phosphate glasses. However, the deeper body color makes these glasses hard for applications. Otherwise, the concentration of  $\text{P}_2\text{O}_5$  introduced into tellurite glasses was very limited, too.  $\text{TeO}_2$  and  $\text{P}_2\text{O}_5$  are well known classic glass network formers. Based on them, many tellurite glass and phosphate glass systems have been investigated and developed for various applications such as laser media, optical amplifier, nonlinear optical devices and biomedical materials [14,15].

The main object is to carry out a detailed study of the effects of the  $\text{P}_2\text{O}_5$  content on the structural, thermal and spectroscopic properties of  $\text{Er}^{3+}$ -doped  $\text{TeO}_2$ – $\text{ZnO}$ – $\text{Na}_2\text{O}$  glasses (TZN) to examine their suitability as potential optical glasses for fiber amplifiers. The influence of temperature and the experimentally determined lifetimes have been discussed. Furthermore, the emission cross-section and the optical gain of the  $\text{Er}^{3+}$ :  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transition was reported.

## 2. Experimental details

Tellurite glasses were prepared according to the following compositions (in mol%): (75) $\text{TeO}_2$ –(20) $\text{ZnO}$ –(4) $\text{Na}_2\text{O}$ –(1) $\text{Er}_2\text{O}_3$  for doped samples (TZNP0), and (71) $\text{TeO}_2$ –(20) $\text{ZnO}$ –(4) $\text{Na}_2\text{O}$ –(4) $\text{P}_2\text{O}_5$ –(1) $\text{Er}_2\text{O}_3$  (TZNP4). The starting materials were from Sigma Aldrich Chemicals with higher purity  $\text{TeO}_2$  (99.9%),  $\text{ZnO}$  (99.9%),  $\text{P}_2\text{O}_5$  (99.9%),  $\text{Na}_2\text{CO}_3$  (99.9%) and  $\text{Er}_2\text{O}_3$  (99.9%). Calculated quantities of the chemical components were mixed in an agate mortar and melted in an electric furnace at 850 °C for one hour in platinum crucibles so that a homogeneously mixed melt was obtained. Immediately after the quench, the glass (as-prepared sample) was annealed at 250 °C (for 1 h) and then slowly cooled to attain ambient temperature. The annealing process was made with the objective of minimizing the internal mechanical stress and obtaining glasses with good mechanical stability. The obtained glasses were cut and polished carefully in order to meet the requirements for optical measurements.

DSC scans of as-cast glass specimens were carried out in Metler Toledo DSC823°. The DSC scans were recorded using 7 mg as-cast glass specimens, which were powdered in order to determine the characteristic glass transition temperatures  $T_g$ , crystallization onset  $T_x$ , and the peak crystallization temperatures  $T_p$ , and heated in a platinum crucible using the same amount of alumina powder as the reference material at the heating rate of 10 °C/min between 200 and 600 °C temperature range. The crucibles used were matched pairs made of platinum and the temperature precision was  $\pm 1$  °C. X-ray diffraction (XRD) patterns were carried out at room temperature in a Philips X'Pert system, using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056$  Å), at 40 kV and 100 mA, the diffractometer setting in the  $2\theta$  range from 15° to 65° by changing the  $2\theta$  with a step size of 0.02°. The Raman spectra were recorded in the 80–1650  $\text{cm}^{-1}$  range using a Jobin–Yvon spectrometer (T64000 model) equipped with an  $\text{Ar}^+$  laser (488 nm exciting line) and a CCD detector in a back-scattering geometry. The sample focalization was controlled by a microscope (x100). The spectra were recorded in two scans (during 100 s) at low power (50 mW) of the excitation line, in order to avoid damage of the glasses. This laser power density was found to optimize the signal-to-noise ratio without over heating the sample. Absorption spectra of these samples were measured in the range 300–1800 nm using a Varian 5000 spectrometer. Up-conversion emission spectra were recorded by exciting the samples at 977 nm at room temperature and down conversion emission were measured under 462 nm at 77 K and room temperature. The photonic excitation at 977 nm was obtained with cw tunable laser diode (LD) with output power up to 1.0 W using a monochromator HR460 and CCD detector for spectra. The photonic excitation at 462 nm with a dye laser (Laser Photonics LN102, PBBO and Coumarine 460) pumped by the pulsed nitrogen laser. The PL time decays were obtained, in the range of

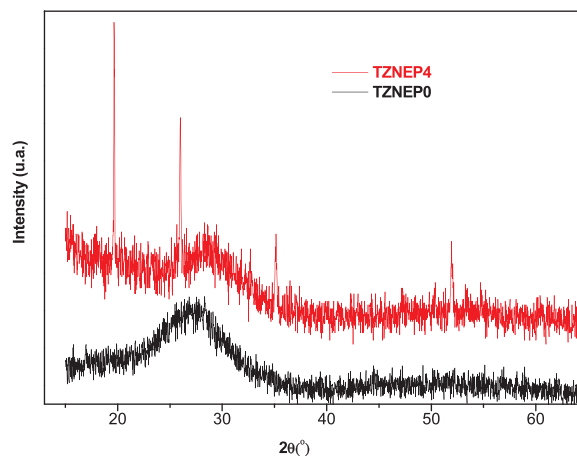


Fig. 1. X-ray diffraction patterns for TZNP0 and TZNP4 samples.

temperature 77 to 300 K, with a monochromator HR460, a PM Hamamatsu R928 and an oscilloscope Nicolet 300 with a time constant of about 20 ns.

## 3. Results and discussion

### 3.1. Structural behavior and thermal stability

The XRD patterns of the glasses not containing  $\text{P}_2\text{O}_5$  (TZNP0) and the samples containing 4 mol% of  $\text{P}_2\text{O}_5$  (TZNP4) are shown in Fig. 1. Starting from the glass sample, these XRD patterns reveal the gradual evolution of various phases with adding of  $\text{P}_2\text{O}_5$ . As can be seen in Fig. 1, the XRD patterns of the TZNP0 samples exhibited a very broad band at  $2\theta$  values ranging between 28° and 54° which indicate typical amorphous clustering of glassy solids. On the other hand, several sharp diffraction peaks, a characteristic of crystalline structure, were clearly observed for the TZNP4 samples, indicating that crystals were successfully precipitated in the glass matrix after adding  $\text{P}_2\text{O}_5$ . The TZNP4 sample presented a broad and high background characteristic of amorphous compounds and a mixture of several crystalline phases. However, the glass state tended to disappear as a result of adding  $\text{P}_2\text{O}_5$ . The patterns obtained from the phosphate glasses show a reduction of the amorphous hump and the development of new peaks corresponding to new phases in addition to the tellurite phase originally present in the sample without  $\text{P}_2\text{O}_5$ . These several sharp diffraction peaks, a characteristic of crystalline structure, were clearly observed after adding  $\text{P}_2\text{O}_5$  to the samples; proof of the presence of additional polycrystalline phase. Phase identification reveals that crystalline peaks can be related to the  $\text{ErPO}_4$  phases [16]. The  $\text{ErPO}_4$  phases had a tetragonal crystal structure with lattice parameters  $a = 6.863$  Å and  $c = 6.007$  Å.

The nanocrystals (NCs) size of the TZNP4 was estimated by the Debye-Scherrer formula [17]:

$$D(\text{nm}) = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where  $k = 0.90$  is the Scherrer constant,  $\lambda = 1.54$  Å is the wavelength of  $\text{CuK}\alpha$  component of the employed copper radiation,  $\beta$  is the full width at half maximum of the diffraction peak at the angle  $\theta$ . The calculated average size of the TZNP4 NCs was estimate to  $D = 36.6$  nm.

The Raman spectra of samples TZNP0 and TZNP4 are shown in Fig. 2. All the spectra have been measured under 488 nm excitation line at room temperature. The evolution of the spectra with varying compositions depicted in the figure can be described using the chemical bonds present and their vibrational frequencies. In the low-frequency region, there is an asymmetric Raman band ranging from 100 to 300  $\text{cm}^{-1}$ , which showed a strong peak at about 110  $\text{cm}^{-1}$ . This peak is attributed to the vibration of the Boson peak [18,19], which was

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