

ENHANCED NEAR-INFRARED EMISSION OF Er^{3+} -DOPED TELLURITE GLASS CONTAINING SILVER NANOPARTICLES

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The broadband luminescence of the Er^{3+} -doped glasses is an excellent optical feature to develop the telecommunication devices. In this report, the effect of silver nanoparticles (NPs) on the near-infrared luminescence properties of Er^{3+} -doped tellurite glasses is studied. The growth of NPs is attained by heat-treatment above the glass transition temperature. Transmission electron microscopic technique revealed the presence of NPs with average size of 14 nm. Under 980 nm excitation wavelength, the broadband of Er^{3+} ions is enhanced by increasing the heat-treatment duration up to 10 h. The involved mechanisms are described to discuss the observed enhancement.

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1. Introduction

Tellurite based glasses show significant structural and optical properties which nominate them as potential materials for various applications in optics, photonics, opto-electronics and telecommunications [1]. The rare earth (RE) solubility of tellurite glasses is higher than silicates and this property as well as high refractive index, low phonon energy, and wide transparency window of tellurite glasses made them known as an interesting glassy host [1,2]. On the other hand, RE-doped glasses show important optical absorption and emission properties which can be applied in various scientific and technological devices [2]. However, increasing the cross-section of such emissions is the challenging issue. In order to overcome this drawback, several methods have been proposed, such as reduction of quenching-centers, incorporation of secondary RE ions, semiconductors, quantum dots or metallic nanoparticles (NPs) in the RE-doped glasses and glass-ceramics [3].

One of the successful proposals to increase the luminescence intensity of RE-doped glasses is the addition of noble metallic NPs, such as gold (Au), silver (Ag), platinum or a combination of them (core-shell NPs) [3–9]. Among the RE ions, the study of emissions in trivalent erbium is of utmost importance since this ion can provide infrared-to-visible upconversion emissions as well as a C-broadband in the telecommunication range, which is of supreme importance to fabricate optical fibers and amplifiers. It has been reported that the

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broadband emission of Er^{3+} ions ($1.53 \mu\text{m}$: $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$) could be altered in the presence of Au and Ag NPs [10–12]. Due to its noteworthy applications, in this paper we report on the influence of silver NPs on near-infrared (NIR) band in an Er^{3+} -doped tellurite glass.

2. Experimental procedures

The glass samples having composition $(75-x-y)\text{TeO}_2-17\text{PbO}-8\text{Na}_2\text{O}-x\text{Er}_2\text{O}_3-y\text{AgNO}_3$ were prepared ($x=0, 0.7$ and $y=0, 1$) by the melt-quenching technique and they are labeled as listed in Table 1. Twenty grams of well-mixed initial reagents consist of tellurium dioxide (TeO_2 , 99%), lead oxide (PbO , 99%), sodium oxide (Na_2O , 99%), erbium oxide (Er_2O_3 , 99.8%), and silver nitrate (AgNO_3 , 99%) were melted at 900°C for 1 h in a platinum crucible. Next, the molten was poured into a pre-heated steel mold at 300°C and annealed for 2 h. All the samples were synthesized by the same procedure and were heat-treated above the glass transition temperature (at 340°C) for different periods (2.5, 10, and 20 h). Samples of same dimensions were polished and cut for optical measurements.

Table 1. Glass compositions (mol%) and their labels, first annealing (HT1, hours) and second heat-treatment (HT2, hours) durations.

Glass label	TeO_2	PbO	Na_2O	Er_2O_3	AgNO_3	HT1	HT2
TPE	74.3	18	7	0.7	0	3	0
TPEA2.5h	73.3	18	7	0.7	1	3	2.5
TPEA10h	73.3	18	7	0.7	1	3	10
TPEA20h	73.3	18	7	0.7	1	3	20
TPA20h	74	18	7	0.0	1	3	20

Transmission electron microscope (JEOL TEM 2100) operating at 200 kV was employed to confirm the presence of silver NPs. The UV-Vis-IR absorption spectra of samples were recorded by a Lambda 20 Perkin-Elmer spectrophotometer with a resolution of 1 nm. Fluorescence spectra were collected using a HORIBA Fluorolog spectrophotometer under 980 nm excitation wavelength provided with its default flash lamp and the signals were collected using a Hamamatsu detector with a resolution of 1 nm. All presented measurements were performed at room temperature.

3. Results and discussion

The glass transition temperature of this glassy system was determined to be $\sim T_g=315^\circ\text{C}$ [13]. Therefore, the glasses are heat-treated at 340°C where the viscosity of the samples is enough to allow the NPs to move, grow, and aggregate. Figure 1 showed the TEM image of the TPEA10h glass sample. The spherical and non-spherical silver NPs are pointed by red arrows and closed circles to highlight them. The size abundance of the observed NPs in this image is shown by the given histogram in the inset. The size of NPs varies between 6 and 22 nm, with an average value of 14 nm. Figure 2 presents the UV-Vis-IR absorption spectra of TPE and TPEA10h glass samples. Seven absorption bands are observed for the glasses containing Er^{3+} ions. The bands are centered at 489, 522, 545, 652, 800, 980 and 1532 nm, corresponding to transitions from ground state ($^4\text{I}_{15/2}$) to various $^4\text{F}_{7/2}$, $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$, $^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$, and $^4\text{I}_{13/2}$ excited states, respectively. In order to observe the surface plasmon resonance (SPR) band of silver NPs, a sample with 0mol% of Er_2O_3 content is prepared by the same procedure. The SPR bands were observed at 438 and 472 nm as shown in the Inset of Fig .2.

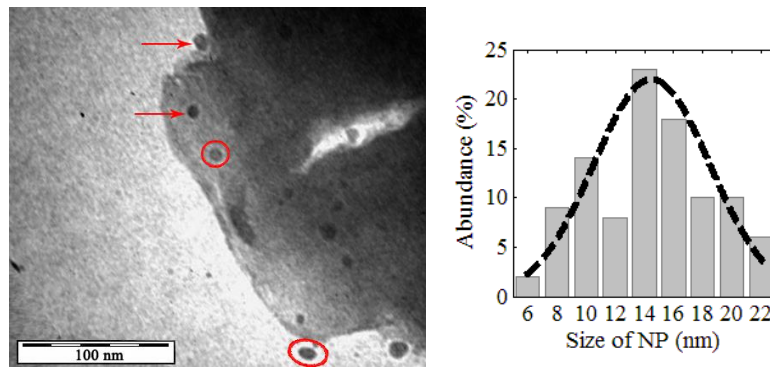


Fig 1. TEM image of the TPEA10h glass sample showing nanoparticles with average size of 14 nm. Inset shows the corresponding size histogram.

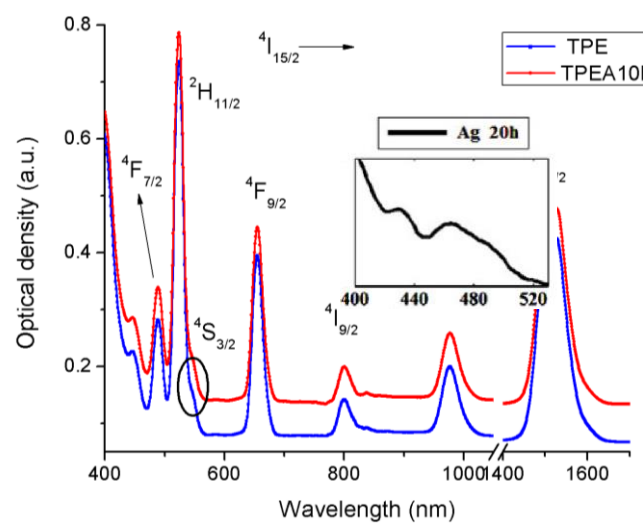


Fig 2. UV-Vis-NIR optical absorption spectra of Er^{3+} -doped glass samples with and without silver NPs. Inset shows the SPR band of Ag NPs in a free- Er^{3+} sample.

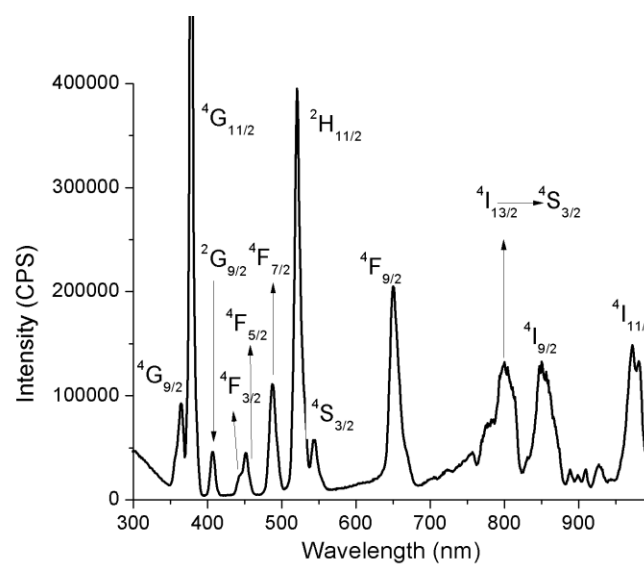


Fig 3. Excitation spectra of Er^{3+} ions doped tellurite glass monitoring the emission at 1530 nm.

Fig. 3 shows the excitation spectrum of sample TPE for the emission at 1.53 μm . As can be seen, the best excitation wavelengths are located at 376, 520, 650 and 980 nm. Due to its potential applications, 980 nm excitation wavelength is selected in the current study. Figure 4.a presents the emission spectra of Er^{3+} -doped tellurite glasses with and without silver NPs in the NIR region. The full-width at half-maximum (FWHM) of this broadband is near 50 nm, and the peak's intensity enhances for 2.3, 4.34, and 3.17 times by increasing the heat-treatments up to 2.5, 10 and 20 hours. The enhanced local field in vicinity of silver NPs and Er^{3+} ions can be the main reason of such enhancements. However, an energy transfer is also probable from particle to ion to enhance the broadband emission. The quenching in the intensity of peak can be associated to the reverse energy transfer from ions to NPs as size of silver NPs increases by time. Silver NPs can also modify the lifetime of the excited states of the RE ions. As given in Figure 4.b, the lifetime of the $^4\text{I}_{13/2}$ level is decreased in the presence of silver NPs. The measured lifetime of the glasses are 2.45, 2.18, 2.00 and 2.08 ms for TPE, TPEA2.5, TPEA10 and TPEA20 glass samples, respectively.

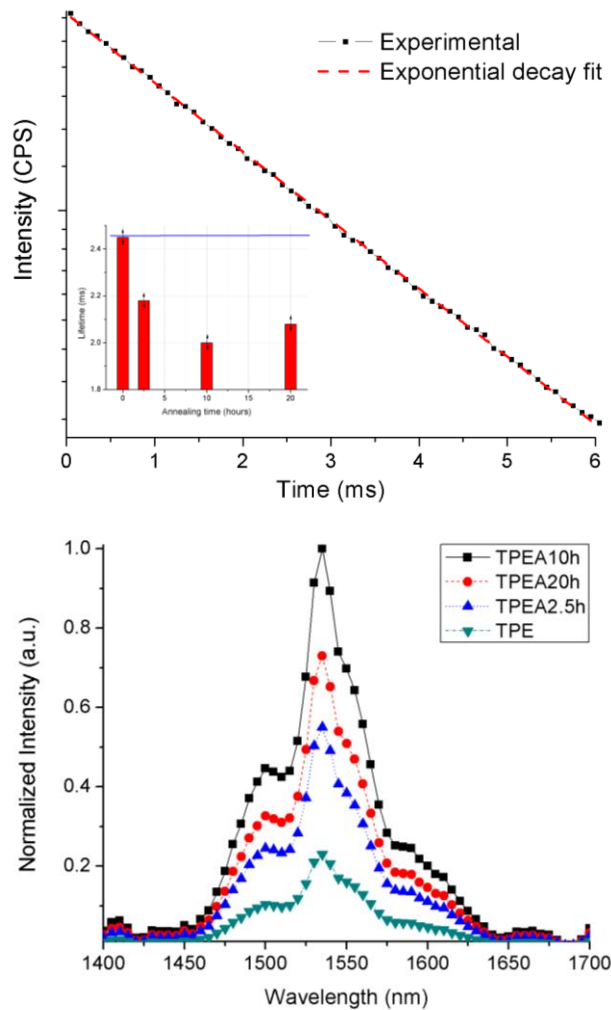


Fig 4. (a) NIR emission spectra of Er^{3+} -doped glasses containing silver NPs after various heat-treatment durations. (b) Variation of lifetime of $^4\text{I}_{13/2}$ excited state of Er^{3+} ions by heat-treatment durations. Inset shows a typical decay profile of transition at 1530 nm.

Fig. 5 shows a partial energy level diagram of the Er^{3+} ion in the vicinity of a silver NP. The NIR emission of Er^{3+} ions ($\sim 1.53 \mu\text{m}$) is a Stokes transition under 980 nm excitation wavelength. In this regard, a 980 nm photon excites the Er^{3+} ion from its $^4\text{I}_{15/2}$ ground state to $^4\text{I}_{11/2}$ excited states where a multiphonon non-radiative relaxation populates the $^4\text{I}_{13/2}$ state. The radiative

transition from latter state to ground state results in the broadband emission at C-band. The luminescence intensity of Er^{3+} -doped tellurite glasses increases by incorporation of heat-treated silver NPs due to localized electric field induced by surface plasmon of NPs. Energy transfer mechanism are also probable in this system between RE ion and metal. The decrease in the lifetime of this level may indicate the energy transfer from particle to ion which enhances the NR luminescence.

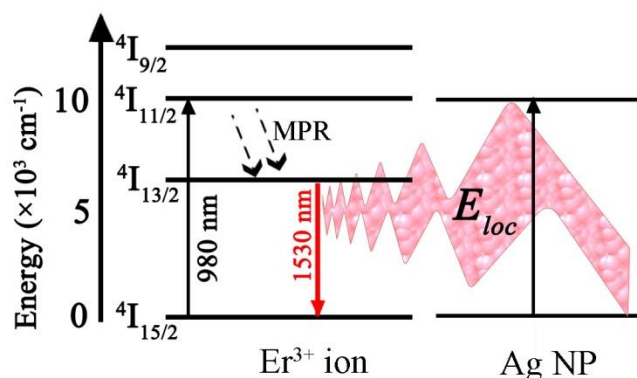


Fig 5. Partial energy level diagram of Er^{3+} ions. MPR= Multi phonon relaxation.

4. Conclusion

The Er^{3+} -doped tellurite glasses containing Ag NPs have been prepared by melt-quenching technique and subsequent heat-treatments. Transmission electron microscopy showed the NPs with average size of 14 nm. After 10 hours of heat-treatments above the glass transition temperature, the band centered at 1530 nm underwent 4.34 times enhancement under 980 nm excitation wavelength. The improvement of the signal in near-infrared region of studied glasses is a promising result to develop several optical devices such as amplifiers, optical fibers, etc.

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