

# Visible upconversion emissions in Pr<sup>3+</sup>-doped TeO<sub>2</sub>–ZnO glass

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Received: 12 November 2011 / Revised: 22 June 2012 / Published online: 16 September 2012  
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**Abstract** The Pr<sup>3+</sup>-doped tellurite zinc oxide (TZO) glasses by conventional melt and quenching technique have been prepared. The absorption spectra of samples doped with different concentrations of triply ionized praseodymium ions have been analyzed. Several upconversion emission bands of the Pr<sup>3+</sup> ions doped in tellurite zinc oxide glasses under 980 nm excitation have been observed. The possible excitation mechanisms responsible for upconversion emissions spanning from blue to near infrared region have been discussed in detail.

**Keywords** Tellurite zinc oxide (TZO) glass · Upconversion · ESA · Superposition

## 1 Introduction

In recent years, there has been a growing research interest in the investigation of optical properties of rare earth elements introduced as doping because of their potential applications in optical devices, upconverters, optical fibers, amplifiers and sensors [1–3]. Among the rare earth ions, triply ionized praseodymium has been intensively studied due to its wide emission spectral range extended from blue to the near infrared (NIR) region of the electromagnetic spectrum [4–15].

Triply ionized praseodymium in crystals and glasses under NIR excitation has been observed to emit radiations

in the visible region [7–9]. The infrared to visible upconversion in Pr<sup>3+</sup>-doped KPb<sub>2</sub>Cl<sub>5</sub> crystal has been studied by Balda et al. [7]. A strong orange and weak blue, green and red upconversion emission bands have been observed under the direct excitation into the <sup>1</sup>G<sub>4</sub> level. Rai et al. [9] have studied frequency upconversion in the Pr<sup>3+</sup>-doped tellurite glass upon excitation at ~816 nm and the most probable channel for the upconversion was excited state absorption (ESA) process. A frequency doubling in Pr<sup>3+</sup> ions doped gallium-lanthanide-sulfide glass by the excitation of 1.319 and 1.064 μm laser pulses has been observed at ~660 and ~532 nm, respectively, with the conversion efficiency of 0.02 % [10]. Choi and co-workers [11] have studied the effect of addition of the Er<sup>3+</sup> in the Pr<sup>3+</sup>-doped selenide glass upon excitation at ~1.48 μm and marked the enhancement in the emission intensity of the Pr<sup>3+</sup> ions caused by the codoping of Er<sup>3+</sup> ions. The optical properties of heavy metal oxide glassy materials codoped with Pr<sub>6</sub>O<sub>11</sub> and silver nanoparticles have been examined on the basis of optical absorbance and luminescence spectra due to the Surface Plasmon interactions [12, 13]. Frequency upconversion in the Pr<sup>3+</sup>-doped TeO<sub>2</sub>-Li<sub>2</sub>O binary glass by the decay curve analysis under 890 nm continuous radiation has been reported [14]. The mechanism responsible for the frequency upconversion emission was observed to be an excited state absorption assisted by the emission of phonons. The photoluminescence studies of Pr<sup>3+</sup> ions doped in lead germanate glass upon direct excitation into the <sup>1</sup>D<sub>2</sub> state using an excitation line of 594 nm from a dye laser pumped by a second harmonic of Q-switched Nd:YAG laser of nanosecond pulses have been reported [15]. The energy transfer process involving the Pr<sup>3+</sup> ions in pairs due to dipole–dipole interaction in the <sup>1</sup>D<sub>2</sub> state has been found to be dominant process for the upconversion emission.

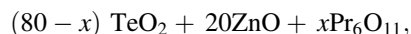
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The search of suitable host materials for the doping of  $\text{Pr}^{3+}$  ions in terms of better optical properties is still in progress. The oxide hosts such as tellurite lead oxide (TPO), lead germanate (PGO), tellurite zinc oxide (TZO), etc. are often described as heavy metallic oxide glasses and these are efficient hosts for the modern world of photonics as they have a broad range of spectral properties such as low loss and long transmission windows. Tellurite glasses have been extensively investigated due to its low cut-off phonon energy, high refractive index, large dielectric constant, high mechanical strength, high chemical durability, non-hygroscopic in nature, high optical damage threshold, small absorption coefficient within the wavelength range of interest and transparent over the visible and NIR regions [16–20]. Tellurite-based glasses with 60–90 mol%  $\text{TeO}_2$  possess a combination of properties, which makes them attractive materials for various photonic applications. They used to combine a wide transmission window (350 nm–5  $\mu\text{m}$ ) with good thermal stability, corrosion resistance and materials with losses of 20 dB/km have been fabricated [21, 22]. Among the heavy metal oxide glasses, tellurite zinc oxide glass is a promising oxide glass host for the photoluminescence applications because of the large band gap (3.37 eV) and an exciton binding energy (60 meV) of zinc oxide [23].

Although the rare earth doped tellurite based glassy materials have been investigated, but to the best of our knowledge there is no such information available about the upconversion properties in TZO glass especially with  $\text{Pr}^{3+}$  ions. In view of this, the present paper deals with the study of frequency upconversion in the  $\text{Pr}^{3+}$ -doped TZO glass under non-resonant excitation corresponding to the  $^3\text{H}_4 \rightarrow ^1\text{G}_4$  transition and mechanism involved in the upconversion emissions have been discussed.

## 2 Experimental

To prepare the  $\text{Pr}^{3+}$ -doped TZO glasses, the used chemical composition of the ingredients viz.  $\text{TeO}_2$ ,  $\text{ZnO}$  and  $\text{Pr}_6\text{O}_{11}$  are the following:



where  $x = 0.3, 0.5, 0.75$  and  $1.0$  mol%.

Various compounds have been thoroughly crushed in an agate mortar to get a homogeneous mixture. The homogeneous mixture was then heated in an alumina crucible using an electric furnace at  $735^\circ\text{C}$  for half an hour. The liquid melt is then air quenched by putting it on a brass plate placed at  $400^\circ\text{C}$ . The melt was then cooled to room temperature to get properly annealed glasses of desired shape and size. Optical absorption spectra of all the doped samples were recorded with a double beam spectrophotometer in the

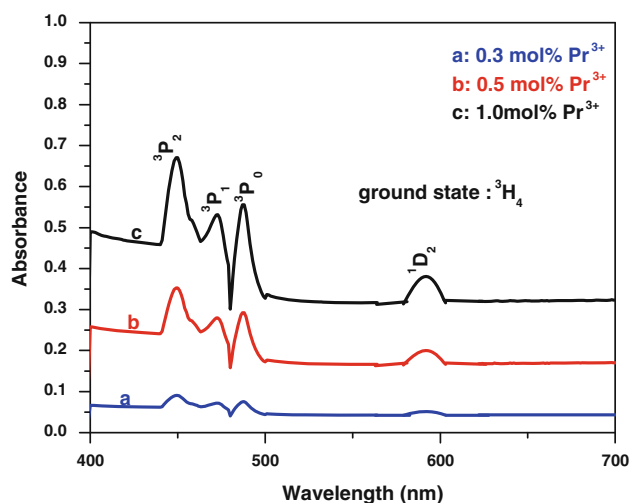
wavelength range of 400–700 nm. For the non-resonant excitation corresponding to the  $^3\text{H}_4 \rightarrow ^1\text{G}_4$  transition of the  $\text{Pr}^{3+}$  ions, a CW diode laser lasing at 980 nm was used. The laser beam was focussed onto the sample with a 10 cm focal length lens. The radiation emitted from the  $\text{Pr}^{3+}$  ions was collected in a direction perpendicular to the incident beam and the signal was analyzed by a monochromator equipped with a photomultiplier tube. All the measurements were done at room temperature.

## 3 Results and discussion

### 3.1 Absorption studies

Figure 1 shows the absorption spectra due to 4f-4f transitions of trivalent praseodymium ions doped in tellurite Zinc oxide glass samples in the spectral range of 400–700 nm. The valence electronic configuration of  $\text{Pr}^{3+}$  ion is  $[5s^25p^64f^2]$ , which designates  $^3\text{H}_4$  as the ground state. The analysis of the observed absorption spectra is summarized as follows:

1. The intensity of absorption peaks increases with increase in the rare earth ion concentrations. For 1.0 mol%  $\text{Pr}^{3+}$ -doped in tellurite zinc oxide glass, the peak intensity is observed to be maximum among all the prepared samples due to the large absorption coefficient.
2. There appear four absorption bands in the 400–700 nm region peaking at  $\sim 450$ ,  $\sim 473$ ,  $\sim 488$ ,  $\sim 591$  nm corresponding to the  $^3\text{H}_4 \rightarrow ^3\text{P}_2$ ,  $^3\text{H}_4 \rightarrow ^3\text{P}_1$ ,  $^3\text{H}_4 \rightarrow ^3\text{P}_0$  and  $^3\text{H}_4 \rightarrow ^1\text{D}_2$  transitions, respectively, assignments are in agreement with the values reported in the other host materials [7, 9, 15, 24]. The absorption transitions



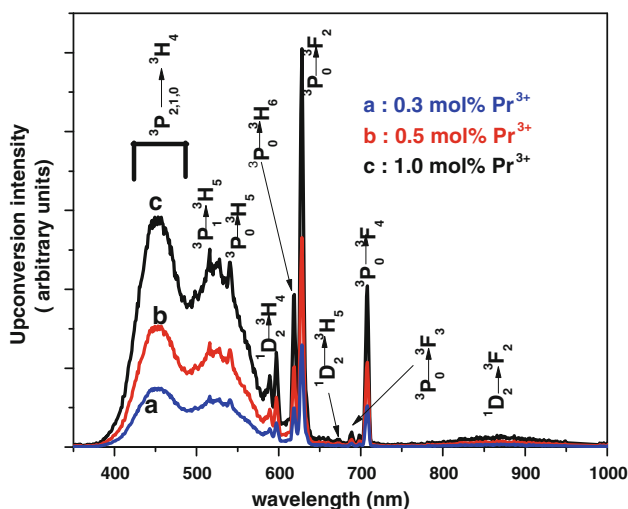
**Fig. 1** Absorption spectra of 0.3, 0.5 and 1.0 mol%  $\text{Pr}^{3+}$  ions doped in TZO glass from 400 to 700 nm wavelength range

are inhomogeneously broadened because of the site to site variations in the strength of crystal field.

### 3.2 Upconversion studies

The upconversion spectra of  $\text{Pr}^{3+}$ -doped in tellurite zinc oxide glasses under non-resonant excitation into the  $^1\text{G}_4$  state using the laser excitation of 980 nm in the 350–1,000 nm region are shown in Fig. 2. There appears several upconversion emission bands peaking at  $\sim 450$ ,  $\sim 528$ ,  $\sim 540$ ,  $\sim 598$ ,  $\sim 620$ ,  $\sim 627$ ,  $\sim 674$ ,  $\sim 690$ ,  $\sim 707$  and  $\sim 866$  nm and attributed to the  $^3\text{P}_{2,1,0} \rightarrow ^3\text{H}_4$ ,  $^3\text{P}_1 \rightarrow ^3\text{H}_5$ ,  $^3\text{P}_0 \rightarrow ^3\text{H}_5$ ,  $^1\text{D}_2 \rightarrow ^3\text{H}_4$ ,  $^3\text{P}_0 \rightarrow ^3\text{H}_6$ ,  $^3\text{P}_0 \rightarrow ^3\text{F}_2$ ,  $^1\text{D}_2 \rightarrow ^3\text{H}_5$ ,  $^3\text{P}_0 \rightarrow ^3\text{F}_3$ ,  $^3\text{P}_0 \rightarrow ^3\text{F}_4$  and  $^1\text{D}_2 \rightarrow ^3\text{F}_2$  transitions, respectively. The broad and intense upconversion emission band in the blue region is due to the contribution of  $^3\text{P}_2 \rightarrow ^3\text{H}_4$ ,  $^3\text{P}_1 \rightarrow ^3\text{H}_4$  and  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transitions. The upconversion intensity of several emission bands is observed to increase with increase in the concentration of  $\text{Pr}^{3+}$  ions.

The log–log plot of the upconversion intensity versus concentration of  $\text{Pr}^{3+}$  ions shows a linear variation (Fig. 3), thereby showing that only one  $\text{Pr}^{3+}$  ion is participating in the upconversion process. To get the information about the number of photons involved in the upconversion emission process, log–log plot of the upconversion intensity versus NIR laser pump power has been made and observed to provide the slope  $\sim 2.09 \pm 0.05$  and  $\sim 2.65 \pm 0.1$  (Fig. 4) for the emissions in the orange and blue regions peaking at  $\sim 598$  and  $\sim 450$  nm, respectively. This confirms the participation of two and three NIR laser photons, which are responsible for the orange and blue upconversion



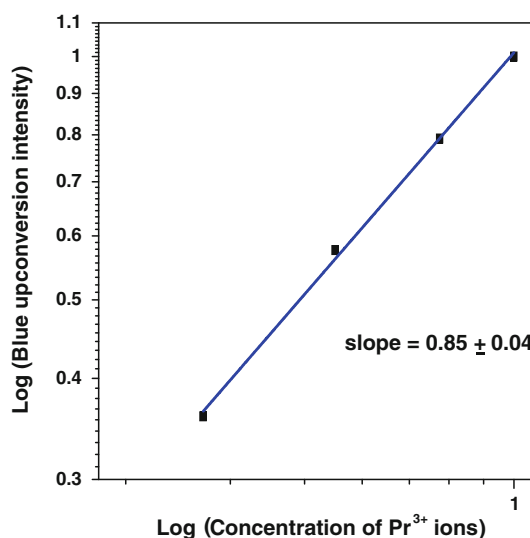
**Fig. 2** Upconversion emission spectra of 0.3, 0.5 and 1.0 mol%  $\text{Pr}^{3+}$ -doped TZO glass from 350 to 1,000 nm wavelength range

emissions, respectively, and hence for the upconversion emission throughout the visible region to occur.

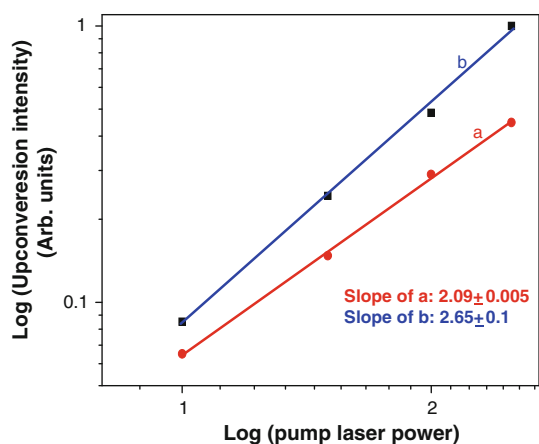
To know the whole mechanism involved in the upconversion emission of  $\text{Pr}^{3+}$ -doped in tellurite zinc oxide glass, we assume the schematic energy level diagram (shown in Fig. 5).

The ground state  $\text{Pr}^{3+}$  ions are excited to the  $^1\text{G}_4$  state through ground state absorption followed by multiphonon emission. The excited  $\text{Pr}^{3+}$  ions in the  $^1\text{G}_4$  state ( $\sim 9,800 \text{ cm}^{-1}$ ) are again pumped through the excited state absorption (ESA) process to a virtual excitation level  $V$  at  $\sim 20,004 \text{ cm}^{-1}$  (Fig. 5), which lies above the  $^1\text{D}_2$  state ( $\sim 16,920 \text{ cm}^{-1}$ ). Since there is no suitable matching of any energy level of excited  $\text{Pr}^{3+}$  ion, excited  $\text{Pr}^{3+}$  ions relax non-radiatively via the emission of four numbers of phonons associated with the lattice vibrations in the host matrix and ultimately the  $^1\text{D}_2$  state is populated. As, the phonon energy of tellurite glass is  $\sim 750 \text{ cm}^{-1}$  [25]. The population in the  $^1\text{D}_2$  state may also be achieved by the following processes.

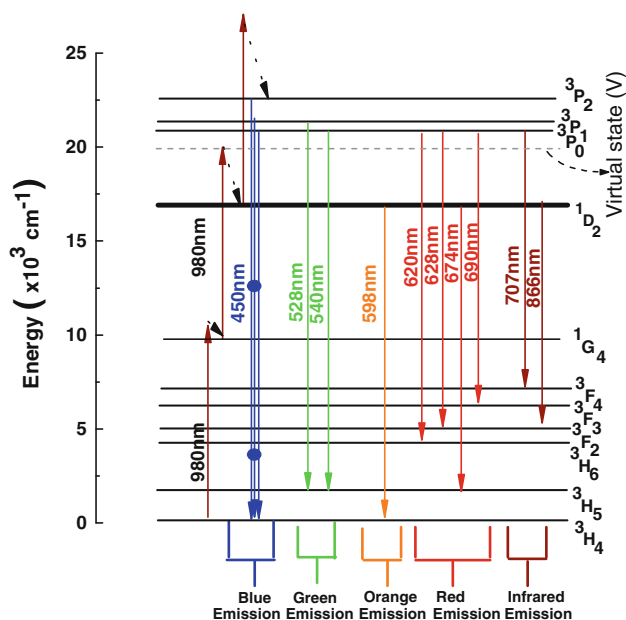
1. *Through energy transfer (ET) between the  $\text{Pr}^{3+}$  ions in the  $^1\text{G}_4$  state:* In this, one ion (acceptor) after receiving the energy from the other ion (donor) in the  $^1\text{G}_4$  state is excited to the higher energy state at  $\sim 19,600 \text{ cm}^{-1}$  and then the other ion (donor) after transferring its excitation energy to the acceptor relaxes to the  $^3\text{H}_5$  state. Thereafter, the acceptor ion returns back to the  $^1\text{D}_2$  state by the multiphonon emission. For this, there should be participation of two  $\text{Pr}^{3+}$  ions, but the log–log plot of upconversion intensity versus rare earth ion concentration provided the slope  $\sim 0.85 \pm 0.04$  (Fig. 3). Thus, there is contribution of only one  $\text{Pr}^{3+}$



**Fig. 3** Log–log plot of blue upconversion intensity and  $\text{Pr}^{3+}$  ion concentration



**Fig. 4** Log–log plot of the upconversion intensities and laser intensity of **a** 598 nm and **b** 450 nm emission



**Fig. 5** Schematic energy level diagram of Pr<sup>3+</sup> ion. The virtual level is shown in dotted straight line and denoted as V

ion. Therefore, the energy transfer process in present case is not a possible source of excitation.

2. *Excited state absorption (ESA) involving Pr<sup>3+</sup> ions in the <sup>3</sup>F<sub>4</sub> state:* As the <sup>3</sup>F<sub>4</sub> level may be sufficiently populated via the nonradiative relaxation from the <sup>1</sup>G<sub>4</sub> state and also through the (<sup>1</sup>G<sub>4</sub>, <sup>3</sup>H<sub>4</sub> → <sup>3</sup>H<sub>5</sub>, <sup>3</sup>F<sub>4</sub>) cross-relaxation energy transfer process, which is again less probable.

Moreover, after non-resonant excitation into the <sup>1</sup>G<sub>4</sub> state, the upconversion emissions from the <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>0</sub> levels are also observed. The energy used to excite the Pr<sup>3+</sup> ions to <sup>3</sup>P states by a consecutive two photon absorption process is not sufficient, because the <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>0</sub> levels

are at ~2,218, ~1,136 and 487 cm<sup>-1</sup> just above the virtual level V at ~ 20,004 cm<sup>-1</sup> attained by the first ESA through the <sup>1</sup>G<sub>4</sub> state (Fig. 5). Also, the <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>0</sub> levels are lying above at the energy gap of ~5,300, 4,220 and 3,570 cm<sup>-1</sup> from the <sup>1</sup>D<sub>2</sub> state. The pump power dependence of the blue upconversion emission around ~450 nm, which is due to superposition of the <sup>3</sup>P<sub>2</sub> → <sup>3</sup>H<sub>4</sub>, <sup>3</sup>P<sub>1</sub> → <sup>3</sup>H<sub>4</sub> and <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>4</sub> transitions, shows cubic behavior with the laser power (Fig. 4). This shows that the upconversion emissions from these <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>0</sub> levels are due to the stepwise absorption of three photons followed by the ESA process.

## 4 Conclusion

The Pr<sup>3+</sup> ions doped in TeO<sub>2</sub>-ZnO glasses have been successfully synthesized by the melt and quenching technique. The NIR to visible upconversion emissions in the Pr<sup>3+</sup>-doped TeO<sub>2</sub>-ZnO glasses have been observed upon non-resonant excitation into the <sup>1</sup>G<sub>4</sub> level. The ESA process is observed to be the dominant one for the emissions throughout the visible region. The broad and intense blue upconversion band centred at ~450 nm is the superposition of the <sup>3</sup>P<sub>2</sub> → <sup>3</sup>H<sub>4</sub>, <sup>3</sup>P<sub>1</sub> → <sup>3</sup>H<sub>4</sub> and <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>4</sub> transitions. The present host materials may be suitable one in making the NIR to visible upconverter.

**Acknowledgments** Authors are very much thankful to Department of Science and Technology, New Delhi, India for providing the financial support.

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