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UV–visible emission in Tb–Yb codoped tellurite glass on 980-nm excitation

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ABSTRACT UV–visible upconversion emission from terbium in a Tb–Yb codoped tellurite glass has been observed on 980-nm excitation. The ultraviolet and violet upconversion emissions involve three photons and the blue, green, yellow, and red emissions arise due to two incident photons. The mechanism involved in these emissions is discussed. The effects of doping concentration and of the sample temperature on the upconversion emissions have also been studied.

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1 Introduction

In recent years, rare earth ion doped glasses have attracted great attention due to their applications in solid-state lasers, display devices, fibers, and online amplifiers [1–3]. Frequency upconversion (UC) of incident infrared radiation to visible/ultraviolet radiation by rare earth doped solids has also been the subject of many studies [4, 5]. Any enhancement of the upconversion efficiency would be of help for this purpose, so modifications in the host and use of a suitable sensitizer to increase the near-infrared absorption have been attempted. The ytterbium ion is one such sensitizer, which has a very large absorption cross section near 10^{-4} cm^{-1} [6]. Energy transfer from the excited Yb^{3+} ions to the emitting rare earth ion species has been shown to cause an improvement in the UC fluorescence intensity [7–9]. Yb^{3+} -sensitized rare-earth systems are known to involve two different mechanisms for upconversion emission [10]. The more efficient mechanism involves energy transfer from an excited Yb^{3+} ion to the acceptor ion. But, if there are no suitable energy levels in the acceptor ion that can receive the excitation energy from an excited single donor, another mechanism, viz. cooperative energy transfer, may take place. In this process a pair of excited Yb^{3+} ions simultaneously transfers its total excitation energy to an acceptor ion in the ground state taking it to an excited level leading to upconverted emissions.

TeO_2 is quite often used as a glass former (in the host glass) because it possesses a relatively high refractive index ($n = 2.1$ to 2.4), good light transmission in the visible and

the infrared regions (up to $7.0 \mu\text{m}$), and its highest phonon frequency ($\sim 800 \text{ cm}^{-1}$) is lower than those for borate, phosphate, silicate, and germanate glasses [11–14]. This lower value of the phonon frequency leads to higher fluorescence efficiency for rare-earth ions in host tellurite glass [15, 16].

In this paper we report the infrared to visible/ultraviolet upconversion emission from Tb^{3+} sensitized by Yb^{3+} , in lithium-modified tellurite glass. The different possible upconversion mechanisms responsible for these emissions are described. We have also studied the concentration dependence of the upconverted emissions. The upconverted emission intensity is seen to decrease with an increase in the temperature of the glass.

2 Experimental details

Rare earth doped tellurite glasses were prepared by the conventional melt and quenching method with the following compositions:



with $x = 1.0, 1.5, 2.0, 2.5$ and $y = 0.0, 1.0, 2.0, 3.0, 4.0, 5.0 \text{ mol } \%$.

Details of sample preparation are described in our other work [17]. Several pieces were prepared for each composition of glass. These were cleaned and polished for optical measurements. All the spectroscopic measurements (except the temperature-dependence study) were performed at room temperature. The emission spectra were obtained by exciting the sample with 980-nm laser radiation from a diode laser. The fluorescence emission was dispersed using a 0.5-m Spex monochromator attached to an IP 21 photomultiplier tube.

3 Results and discussion

3.1 Emission properties and cooperative energy transfer from Yb^{3+} ions to Tb^{3+} ions

Pure Tb^{3+} doped in tellurite glass gives no fluorescence on excitation with 980-nm laser light, as there is no absorption at this energy. Even a small amount of Yb^{3+} added to the glass however results in intense fluorescence from Tb^{3+} ions. Figure 1 shows a fluorescence spectrum of Tb^{3+} on excitation at 980 nm in the presence of Yb^{3+} . The observed emission bands are assigned as 487 nm ($^5D_4 \rightarrow ^7F_6$), 545 nm ($^5D_4 \rightarrow ^7F_5$), 585 nm ($^5D_4 \rightarrow ^7F_4$), 624 nm ($^5D_4 \rightarrow ^7F_3$),

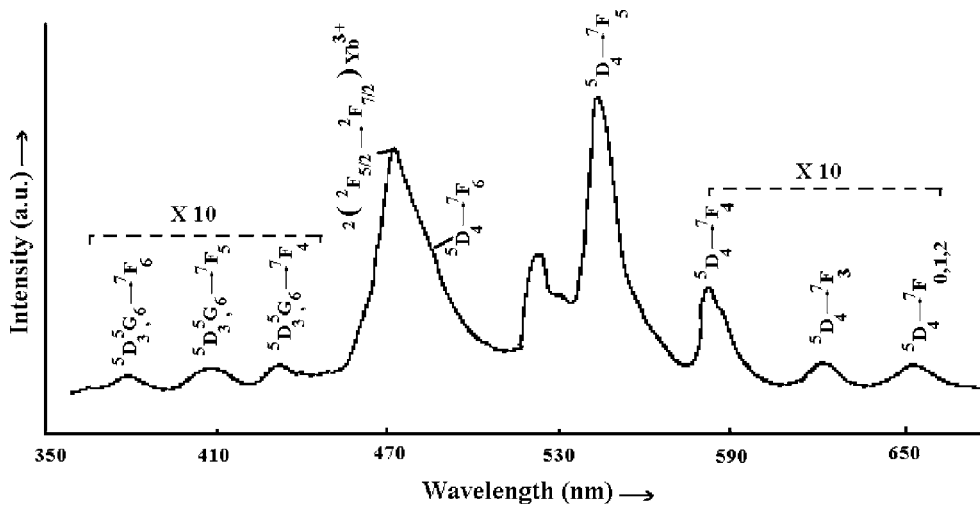


FIGURE 1 Upconversion spectrum of the Tb^{3+} ion in Tb^{3+} - Yb^{3+} codoped tellurite glass under 980-nm excitation at room temperature

and 656 nm (${}^5D_4 \rightarrow {}^7F_{0,1,2}$). The emission band observed at 476 nm is assigned to the cooperative emission from a pair of Yb^{3+} ions in the ${}^2F_{5/2}$ state [18]. The energy levels of Tb^{3+} and Yb^{3+} ions (up to an excitation energy of $30\,000\text{ cm}^{-1}$) are shown schematically in Fig. 2. It is obvious that the incident radiation can excite only the ${}^2F_{5/2}$ state of Yb^{3+} . It is seen from this that the total excitation energy of a pair of Yb^{3+} ions, each excited to the ${}^2F_{5/2}$ state, matches closely that of the 5D_4 state of a Tb^{3+} ion. Thus, energy transfer from a pair of excited Yb^{3+} ions to an unexcited Tb^{3+} ion can populate the latter's 5D_4 state quite efficiently. Radiative decay of this state to the various components of the ground 7F state of Tb^{3+} yields the above bands.

When the concentration of Yb^{3+} ions in the codoped glass is increased there appear additional bands in the UV–violet regions. These bands are also due to Tb^{3+} ions and are assigned to the transitions ${}^5D_3, {}^5G_6 \rightarrow {}^7F_6$ (380 nm), ${}^5D_3, {}^5G_6 \rightarrow {}^7F_5$ (409 nm), and ${}^5D_3, {}^5G_6 \rightarrow {}^7F_4$ (433 nm). These bands have also been observed recently in Tb–Yb codoped silica sol–gel and fluoroindate glasses [19, 20]. Studies of the input power dependence of all the observed bands indicate that blue, green, yellow, and red bands involve a two-incident-photon process, while the ultraviolet–violet bands involve three incident photons.

Observation of upconverted emission covering the spectral range from ultraviolet to red has led us to propose the following excitation schemes (see Fig. 2). Since the energy of the incident photon equals the excitation energy of the Yb^{3+} ${}^2F_{5/2}$ level, it excites Yb^{3+} ions from the ground ${}^2F_{7/2}$ level to the ${}^2F_{5/2}$ level. Two excited Yb^{3+} ions in the ${}^2F_{5/2}$ level cooperatively transfer their total excitation energy to a neighbouring Tb^{3+} ion in its ground state, exciting this Tb^{3+} ion to the 5D_4 multiplet [19, 21, 22]. The excited Tb^{3+} ions radiatively relax to the lower states ${}^7F_6, {}^7F_5, {}^7F_4, {}^7F_3$, and ${}^7F_{0,1,2}$ giving the five emission bands at 487, 545, 585, 624, and 656 nm, respectively. It is seen from Fig. 1 that the emission in the blue region has two peaks at 487 nm and 476 nm. The peak at 487 nm is ascribed to ${}^5D_4 \rightarrow {}^7F_6$ (Tb^{3+}) and at 476 nm is interpreted as due to the cooperative emission of Yb^{3+} , in which the total excitation energy of the pair is emitted in a single photon.

The other three emission bands at 380 nm, 409 nm, and 433 nm are observed at higher concentrations of Yb^{3+} (above 2 mol %) and are probably due to the following mechanism. The Tb^{3+} ions already in the 5D_4 level are excited to the 5D_1 level by absorption of an incident photon of 980 nm (excited state absorption (ESA) process). It is also possible that an excited Yb^{3+} ion in its ${}^2F_{5/2}$ level transfers its energy to

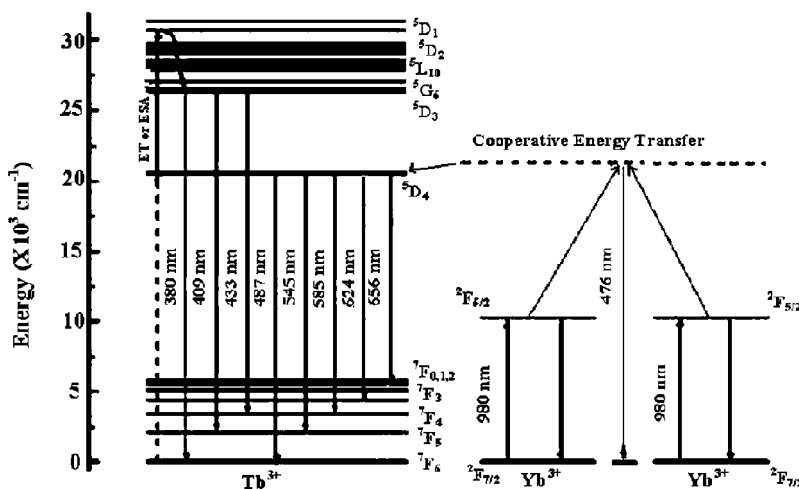


FIGURE 2 Simplified energy-level diagrams of Tb^{3+} and Yb^{3+} ions and possible mechanisms for frequency upconversion under 980-nm excitation

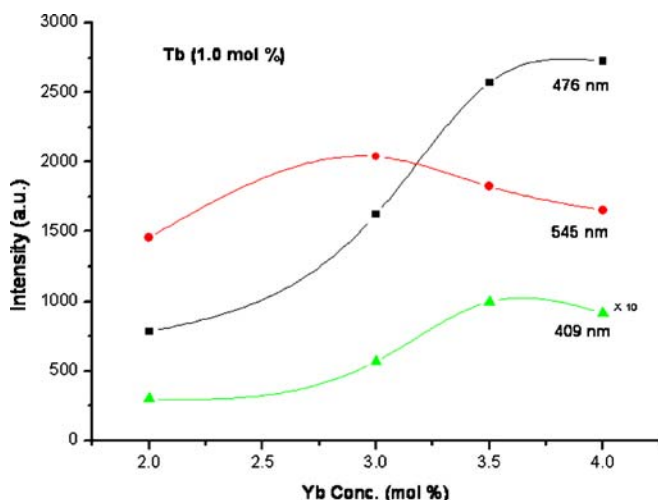


FIGURE 3 Dependence of emission intensity of bands at 409 nm, 476 nm, and 545 nm with the variation of Yb^{3+} ion concentration. Concentration of terbium ions is fixed at 1.0 mol %. Intensity of emission at 409 nm is increased 10 times in the graph

an adjacent Tb^{3+} ion in the 5D_4 level to take it to the 5D_1 level (energy transfer (ET) process). A triad of excited Yb^{3+} ions each in the $^2F_{5/2}$ state may also cooperatively transfer their energy to a Tb^{3+} ion in the ground state and excite it to the 5D_1 state (see below). The existence of a large number of energy levels between the 5D_1 and 5D_3 levels of Tb^{3+} (see Fig. 2) leads to a fast non-radiative decay to the lowest-lying levels in this group of levels, i.e. 5D_3 and 5G_6 , from which radiative transitions can arise, as seen at 380, 409, 433 nm due to the transitions $^5D_3, ^5G_6 \rightarrow ^7F_6, ^5D_3, ^5G_6 \rightarrow ^7F_5$, and $^5D_3, ^5G_6 \rightarrow ^7F_4$, respectively. If a triad of Yb^{3+} ions each in the $^2F_{5/2}$ state are acting cooperatively an emission at 333 nm would appear. This emission is not seen. Glasses, even those with low phonon frequency lattices doped only with Yb^{3+} ions, also do not show any evidence of the existence of such triads of excited ions and their role in cooperative energy

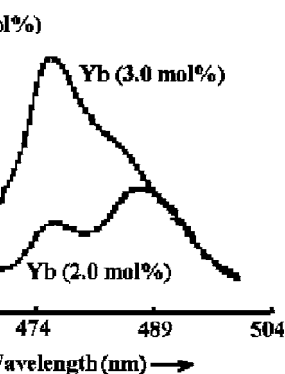
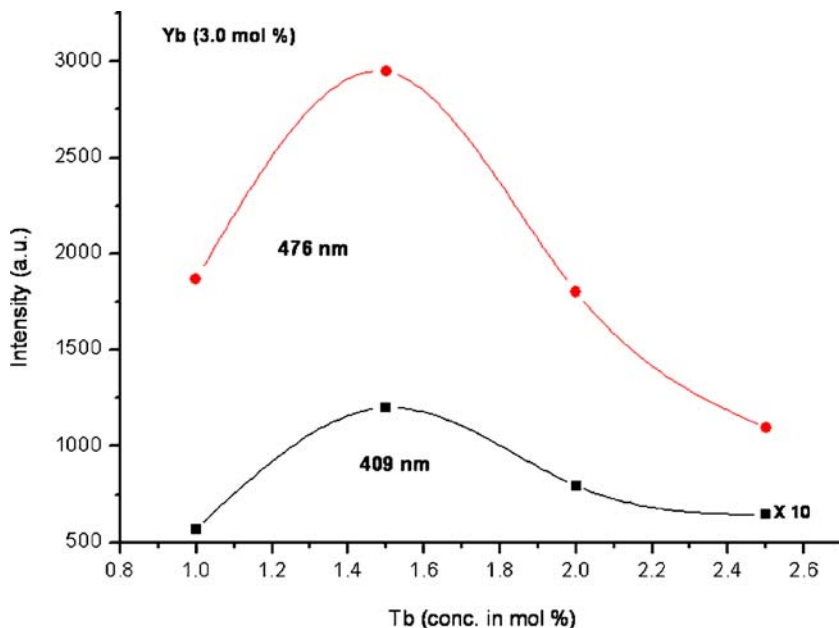


FIGURE 4 Effect of ytterbium ion concentration on the intensity of cooperative emission at 476 nm at a fixed concentration of terbium ions. A blue shift implies that cooperative energy transfer dominates for higher concentrations of ytterbium ions

transfer to populate the 5D_1 level of the Tb^{3+} ion is ruled out in the present Tb^{3+} – Yb^{3+} codoped samples.

3.2 Concentration-dependence study of Tb^{3+} emissions

In order to verify the processes suggested, the dependence of the Tb^{3+} emission intensity on the concentrations of Tb^{3+} and Yb^{3+} was studied, keeping the input laser power constant. Earlier studies on Tb^{3+} -doped tellurite glass had shown that the fluorescence intensity in a tellurite host is maximum for a 1.0 mol % concentration of Tb^{3+} [23]. Therefore, initially the concentration of the Tb^{3+} ion was kept fixed at 1.0 mol % and that of Yb^{3+} was changed (2.0, 3.0, 3.5, and 4.0 mol %). The fluorescence emission was monitored for all samples with these concentrations. The emission intensity was maximum for the sample with the composition 1.0 mol % Tb^{3+} + 3.0 mol % Yb^{3+} . Any further increase of Yb^{3+} concentration causes a reduction in the intensity of the visible fluorescence emissions. But, the intensity of the

FIGURE 5 Effect of terbium ion concentration on the intensity of emission of bands at 409 nm and 476 nm with fixed concentration of ytterbium ions at 3.0 mol %

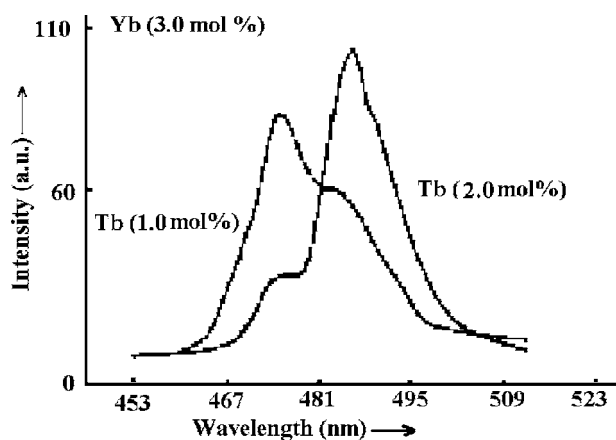


FIGURE 6 Variation in intensity of the Tb^{3+} ion peak at 487 nm on changing the terbium ion concentration at a fixed concentration of Yb^{3+} ions

UV and violet bands reaches its maximum for higher Yb^{3+} concentrations. Figure 3 shows the increase in intensity of the blue emission from Yb^{3+} and the violet emission from Tb^{3+} on increasing the Yb^{3+} concentration. The two curves are almost parallel. This supports the suggestion that the population of the 5D_1 level of Tb^{3+} takes place through energy transfer (ET) from a third Yb^{3+} ion to excite a Tb^{3+} ion in the 5D_4 level. The observed reduction of the intensity of the (${}^5D_4 \rightarrow {}^7F_5$) green emission is because, with the number of emitting ions fixed, any increase in the population of the 5D_1 level will reduce the population of the 5D_4 level (Fig. 3). Further, the intensity of the 476-nm peak is increased due to an excess of Yb^{3+} relative to that of the 487-nm peak and the blue (composite) peak in the emission shows a blue shift (Fig. 4).

Further, in order to study the dependence of fluorescence emission on terbium ion concentration the concentration of Yb^{3+} was kept fixed at 3.0 mol % and that of Tb^{3+} was varied. The emission intensity is seen to be maximum for a glass with Yb^{3+} (3.0 mol %) + Tb^{3+} (1.5 mol %) composition. The Tb^{3+} concentration dependence of the intensities of the 409-nm and 476-nm bands is shown in Fig. 5. The composite blue peak is again seen at 483.0 nm (Fig. 6). Any further increase of Tb^{3+} concentration results in a decrease in intensity of all the emission bands. If we fix the concentration of Tb^{3+} (2.0 mol %) and increase the concentration of Yb^{3+} to 3.0, 4.0, and 5.0 mol % the emission intensity of the 409-nm band increases further. It becomes quenched further for 2.5 mol % of Tb^{3+} .

Thus, concentration-dependence studies of fluorescence intensity reveal that energy transfer from excited Yb^{3+} ions to Tb^{3+} ions already in the 5D_4 level is the most likely mechanism for populating the Tb^{3+} 5D_3 and 5G_6 levels. However, a small contribution due to ESA cannot be ruled out as a large input power (600 mW) was used for these excitations.

3.3 Temperature-dependence study of Tb^{3+} emissions

The temperature dependence of Tb^{3+} emissions containing different concentrations of Yb^{3+} and Tb^{3+} was in-

vestigated. A decrease in the intensity of all the emissions was observed when the temperature was increased. The rate of decrease of intensity of bands involving the 5D_3 level is seen to be larger compared to that for emissions from the 5D_4 level.

4 Conclusion

UV-visible upconversion emissions have been observed in the Tb^{3+} ion in lithium-modified tellurite glass codoped with Tb^{3+} and Yb^{3+} ions on infrared excitation at 980 nm. A concentration-dependence study of Tb^{3+} - Yb^{3+} emission reveals that energy transfer from the excited Yb^{3+} to the excited Tb^{3+} (5D_4) ion is responsible for UV-violet emissions. It is also found that the emission intensity of all the bands decreases with increase of temperature.

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