Effect Of Introducing ZrO$_2$ On The Upconversion Emission Of Tellurium Tungstate Glass

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Abstract. The present study reports the influence of incorporating ZrO$_2$ on the upconversion emission intensity of Er$^{3+}$/Yb$^{3+}$ doped/codoped TeO$_2$-WO$_3$ glasses prepared via melt-quenching technique. The amorphous nature of the glasses has been confirmed from the XRD analysis. The possible mechanisms responsible for boosting the UC emission intensity have been explained from the pump power-based UC analysis and suitable energy level diagram. The colour purity and colour-tunability have been analyzed by the CIE chromaticity diagram.

INTRODUCTION

Among the various types of upconverting (UC) materials, the rare-earth doped glasses form an important class. The rare-earth doped upconverting glasses have a variety of applications in the modern world like optical fiber amplifiers, solid-state lighting, optical temperature sensing, solar-cells, bioimaging, etc. [1, 2]. There are several kinds of glasses like silicate, phosphate, germanate which serve as suitable hosts, but the glasses having TeO$_2$ as a former proves superior to the other ones. This is because the TeO$_2$ based glasses have relatively low phonon frequency and high refractive index which reduces the non-radiative relaxations, thereby increasing the upconversion emission intensity. Other than these, the tellurite glasses have good mechanical strength and can incorporate large amount of rare-earth ions [3].

Although TeO$_2$ is the main component (former), it cannot form glass by its own. It requires modifiers like Bi$_2$O$_3$, Pb$_2$O$_4$, WO$_3$, B$_2$O$_3$, P$_2$O$_5$, etc. to form a glass network. Among distinct number of glass modifiers, the heavy metal oxides are found to be the most suitable ones. The metal oxides having mass density $> 5$ gm/cc are called as heavy metal oxides. One such heavy metal oxide is ZrO$_2$. The present article explores the consequence of introducing ZrO$_2$ on the upconversion emission of Er$^{3+}$/Yb$^{3+}$ doped/codoped TeO$_2$-WO$_3$ (TW) glass matrix. The upconversion emission spectra of Er$^{3+}$/Yb$^{3+}$ doped/codoped TeO$_2$-WO$_3$ glass has been recorded before and after the incorporation of ZrO$_2$ (TWZr) using 980 nm diode laser excitation. The enhancement in the upconversion emission intensity and main mechanisms involved in them has been explained thoroughly.

SYNTHESIS OF SAMPLE AND CHARACTERIZATIONS

All the glasses have been synthesized using melt-quenching technique. The precursors TeO$_2$ (Sigma Aldrich, 99.99%), WO$_3$ (Chemical Drug House, 99.9%), ZrO$_2$ (Chemical Drug House, 99.9%), Er$_2$O$_3$ and Yb$_2$O$_3$ (Chemical Drug House, 99.9%) have been taken according to following compositions,

(80.0-x) TeO$_2$ + 20.0 WO$_3$ + x Er$_2$O$_3$
where, $x = 0.3$, 0.6 and 1.0 mol%

(79.4-y) TeO$_2$ + 20.0 WO$_3$ + 0.6 Er$_2$O$_3$ + y Yb$_2$O$_3$
where, $y = 1.5$, 2.0 and 2.5 mol%

67.4 Te TeO$_2$ + 20.0 WO$_3$ + 10.0 ZrO$_2$ + 0.6 Er$_2$O$_3$ + 2.0 Yb$_2$O$_3$

The optimized concentrations of Er$^{3+}$/Yb$^{3+}$ have been found to be 0.6/2.0 mol%. The precursors were ground properly with the help of mortar and pastel. After that, the obtained mixture was kept inside the muffle furnace at 875 $^\circ$C. Finally, the glass melt was poured into a pre-heated brass mould for quenching. The final product obtained has been polished to get the glasses ready for further investigation. The upconversion emission spectra has been
recorded using a setup comprising of a continuous-wave 980 nm diode laser of variable power and a detector having a photo-multiplier tube.

RESULTS AND DISCUSSIONS

Structural Analysis

The XRD spectra of the optimized doped/codoped glasses have been shown in fig. 1. The absence of any sharp diffraction peak confirms the amorphous nature of the synthesized glasses.

FIGURE 1.XRD plot of 0.6 mol% Er\(^{3+}\) doped TW; Er\(^{3+}/Yb\(^{3+}\) codoped TW and TWZr glasses

Upconversion Emission Study and Involved Mechanisms

The upconversion (UC) emission spectra of 0.6/2.0 mol% Er\(^{3+}/Yb\(^{3+}\) doped/codoped TW and TWZr glasses have been recorded in the spectra range of 400-700 nm using 980 nm continuous wave diode laser excitation. As shown in Fig. 2(a), all the doped/codoped glasses show three visible emission peaks situated at ~ 525 nm (green), ~ 547 nm (green) and ~ 657 nm (red). These emission peaks can be attributed to the \(^2\)H\(^{11/2}\)→\(^4\)I\(^{15/2}\), \(^4\)S\(^{3/2}\)→\(^4\)I\(^{15/2}\) and \(^4\)F\(^{9/2}\)→\(^4\)I\(^{15/2}\) transitions of the Er\(^{3+}\) ion respectively [4]. At 151 mW laser power, the green emission intensities of the Er\(^{3+}/Yb\(^{3+}\): TW and Er\(^{3+}/Yb\(^{3+}\): TWZr glasses boosted up by ~ 24 and ~ 33 times respectively as compared to the Er\(^{3+}\): TW glass. Similarly, at the same laser power, the red emission intensities of Er\(^{3+}/Yb\(^{3+}\): TW and Er\(^{3+}/Yb\(^{3+}\): TWZrcodoped glasses gets enhanced by ~ 118 and ~ 141 times respectively as compared to the doped glass.

In order to get a proper idea of the possible UC mechanisms, the pump power dependent UC emission analysis of 0.6/2.0 mol% TWZr glass has been performed according to the following equation [5],

\[ I_{UC} = k \cdot (P_{UC})^n \]

where, ‘\(I_{UC}\)’represents the integrated emission intensities, ‘k’ is a constant of proportionality, ‘\(P_{UC}\)’ is the laser power and ‘n’ is the number of excitation photons responsible for a particular UC emission band. From the ln-ln plot of equation (1), the value of ‘n’ for green and red bands comes out to be ~ 1.50 and ~ 1.25 respectively {Fig. 2(b)}. The values of ‘n’ make it clear that both the UC emission bands are a result of two-photon absorption process. However, the calculated slope values are less than 2 because of the involvement of other significant processes like ground-state absorption (GSA), excited-state absorption (ESA), energy transfer (ET), non-radiative relaxations, etc. [4, 5].

The various possible UC mechanisms have been shown in the energy level diagram {Fig. 3}. In the Er\(^{3+}\) doped TW glass, the green emissions take place due to GSA and ESA1 processes and the red emission take place due to GSA and ESA2 process. As the green emission intensity is very much greater than the red emission intensity, it can be concluded that a major part of electrons are excited to \(^2\)F\(^{3/2}\) energy level and only a few electrons relaxes non-radiatively to \(^4\)I\(^{13/2}\)level energy level and then populate the \(^4\)F\(^{9/2}\) energy level through ESA2 process. In addition to the absorption processes, the ET processes are mainly responsible for intense UC emission bands {see Fig. 2}. The sensitizer (Yb\(^{3+}\)) ion having larger absorption cross-section around 980 nm as compared to the Er\(^{3+}\) ion, absorbs a larger number of 980 nm excitation photons. After that, the Yb\(^{3+}\) ion transfers the absorbed energy to various energy levels of Er\(^{3+}\) via ET\(_1\), ET\(_2\) and ET\(_3\) processes thereby causing increment in the UC emission intensities [6]. After incorporating ZrO\(_2\), the green and red emissions get more intensified, this is because of the modification in the ligand field around the activator (Er\(^{3+}\)) ion [2, 7, 8].
FIGURE 2. (a) UC emission spectra of 0.6/2.0 mol% Er\textsuperscript{3+}/Yb\textsuperscript{3+} doped/codoped TW, TWZr glasses (b) Pump power analysis of UC emission spectra of TWZr glass.

FIGURE 3. Suitable energy level diagram of Er\textsuperscript{3+}/Yb\textsuperscript{3+}codoped system

CIE Colour Coordinate Study

The colour coordinates of 0.6 mol% Er\textsuperscript{3+}: TW, 0.6/2.0 Er\textsuperscript{3+}/Yb\textsuperscript{3+}: TW and 0.6/2.0 mol%: Er\textsuperscript{3+}/Yb\textsuperscript{3+}: TWZr glasses have been determined from the CIE chromaticity diagram (Fig. 4(a)). All three doped/codoped glasses have colour coordinated situated at (0.27, 0.71) which falls in the green region. Also, the pump power dependent CIE study of the 0.6/2.0 mol%: Er\textsuperscript{3+}/Yb\textsuperscript{3+}: TWZr glass shows that the glass does not exhibit colour tunability {see Fig. 4(b)}. The colour purity of 0.6/2.0 mol%: Er\textsuperscript{3+}/Yb\textsuperscript{3+}: TWZr glass has been calculated at different pump powers using the following expression [9],

\[
\text{Colour Purity} (\%) = \left( \frac{(X_s-X_i)^2+(Y_s-Y_i)^2}{(X_d-X_i)^2+(Y_d-Y_i)^2} \right) \times 100\%
\]  

(2)

where, (X\textsubscript{s}, Y\textsubscript{s}), (X\textsubscript{d}, Y\textsubscript{d}) and (X\textsubscript{i}, Y\textsubscript{i}) denote the sample point, dominant point and illumination point respectively. The value of illumination point is fixed and equal to (0.3101, 0.3162). The average colour purity as calculated from equation (2) comes out to be \(~97\%\). The highly pure and non-colour tunability makes the ZrO\textsubscript{2} modified codoped glass suitable for solid-state lighting and NIR to visible upconverters.
CONCLUSIONS

The Er\(^{3+}\)/Yb\(^{3+}\) doped/codoped TW and TWZr glasses have been synthesized by melt-quenching method. After incorporating ZrO\(_2\) as modifier, additional increment has been witnessed in the UC emission of the Er\(^{3+}\)/Yb\(^{3+}\) doped/codoped TW glass due to modification in the crystal field around the Er\(^{3+}\) ion. Also, the CIE study shows, that the Er\(^{3+}\)/Yb\(^{3+}\) codoped TWZr glass possess non-tunable and highly pure green emission (~ 97%). Thus, the synthesized glass can be utilized in manufacturing NIR to visible green upconverters and solid-state lighting applications.

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