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Enhanced Green Light Upconversion in Terbium–Ytterbium ions Co-doped Zinc–Tellurite Glasses

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Abstract

Transparent zinc-tellurite glasses co-doped with Terbium ion (Tb^{3+}) and Ytterbium ion (Yb^{3+}) were successfully created using the melt-quench method in an air environment. Systematic investigations were conducted using X-ray diffraction, differential scanning calorimeter, UV-Visible-IR, and upconversion spectra to examine the structural, thermal, and optical properties. The absorption peaks from the Tb^{3+} transitions are located at 486 nm ($^7F_6/^5D_4$) in the Tb^{3+} single doped glass. The overlapping absorption bands are believed to be the result of the transition from $^5D_0$ to $^3H_7$ excited-state levels were observed. Under 978 nm laser stimulation, a zinc tellurite glass sample containing Tb^{3+} and Yb^{3+} ions showed strong, typical Tb^{3+} emissions ($^5D_4$-$^7F_{3-6}$ and $^5D_3$-$^7F_{4-6}$). The upconversion's laser power dependence demonstrated that the two-photon process was in charge of the green emission.

Key words : Upconversion; tellurite glasses: absorption spectra.

1. Introduction

Due to its superior qualities over traditional luminous materials, lanthanide (Ln) ion doped transparent glass ceramics, which are produced by carefully regulating the nucleation and development of nanocrystals in precursor glasses, have been extensively studied in recent decades[1–7]. Their qualities,

which include easier manufacturing processes, improved thermal stability, reduced production costs, and favorable crystal environments for RE ions, are carried over from both glasses and crystals[7-9]. Fluoride nanocrytal-based transparent oxyfluoride glass ceramics have garnered significant interest among different types of glass ceramics because they combine the benefits of low phonon energy environments of fluoride nanocrytals with the superior chemical and mechanical stability of oxide glasses[6–8]. As a result, a great deal of research has been done on the creation, down-conversion, and up-conversion luminescence in Ln ion doped oxyfluoride glass ceramics[7-8]. In upconversion materials, Ln ions such Er^{3+}, Tm^{3+}, and Ho^{3+} are frequently doped as luminescent centres. When exposed to near-infrared (NIR) light, these ions produce upconversion luminescence[10–14]. Because Yb^{3+} ions have a large absorption cross section of approximately 978 nm and can effectively transfer the excitation energy to other Ln ions, they are well known for enhancing the optical pump efficiency of these luminous centers[12–13]. In particular, a thorough investigation has been conducted into the upconversion properties in Er^{3+} [7], Er^{3+},Yb^{3+} [6,18], and Tm^{3+},Yb^{3+} [16] doped glass ceramics. Only a small number of research, meanwhile, concentrated on Tb^{3+}–Yb^{3+} co-doped glass ceramics[8].

This work effectively synthesized Tb^{3+}–Yb^{3+} co-doped Zinc-Tellurite glasses and thoroughly examined their upconversion characteristics and processes. Our findings demonstrated that green upconversion was caused by a two-photon mechanism involving cooperative energy transfer from two Yb^{3+} ions to one Tb^{3+} ion.

2. Experiment

Glass samples with nominal composition of TNZTY≡69%TeO_2- 10%Na_2CO_3–20%ZnO–0.5%Tb_2O_3–0.5%Yb_2O_3 (in mol%) was prepared by the melt-quenching method in air atmosphere. TeO_2(99%), Na_2CO_3(97%), ZnO(99.3)–Tb_2O_3(99%)–Yb_2O_3(99%) (all from Otto Chemei) were used as raw materials. The raw materials were thoroughly pulverized with the use of a pestle and mortar and meticulously weighed using a sophisticated digital balance. After being placed in an alumina crucible, the chemicals were melted in air for one hour at 980 °C. To create precursor glass, the melt was poured over a stainless-steel plate and then compressed by another plate. The produced samples were then heated to 330°C for two hours. After optical polishing, the sample was given the moniker TNZTY. X-ray diffraction (XRD) patterns were run on a Rigaku Smart Lab 9kW device in order to do additional characterisation. DCS was performed for the thermal investigations using PerkinElmer's DSC6000. Using a RI Fiber Optic Spectrometer (Research India), UV-VIS-IR spectra were measured. Spectra of upconversion were measured using Jobin Vyon-Fluorolog and Horriba. At room temperature, each measurement was completed.

Results and discussion

DSC (Differential Scanning Calorimetry) :

DSC plot of TNZTY glass sample is carried by by using DSC6000, PerkinElmer. in temperature range 50 to 400 , the Scanning rates were kept 0.1 ºC. The thermal plot between heat flow and

temperature is shown in fig. 1. The glass transition temperature of the TNZTY is observed 310 .

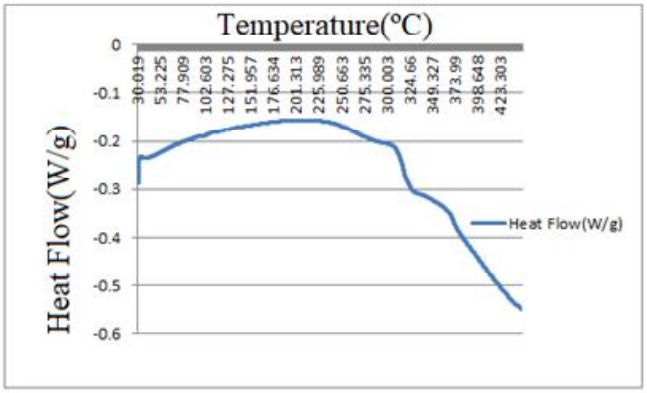

Fig. 1, DSC plot of TNZTY sample

XRD (X-ray Diffraction) :

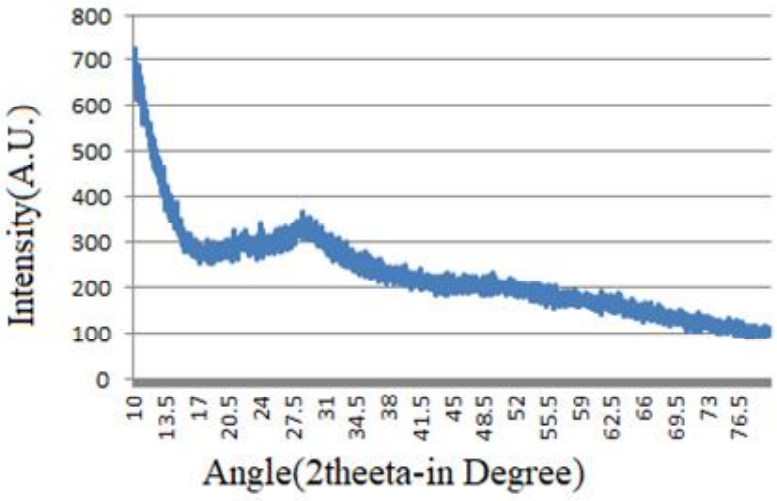

Fig. 2, X-ray Differactogram of TNZTY Sample

Figure 2 exhibit x-ray differactogram of TNZTY sample in double of diffraction angle range 10º to 80º. The plot dose not has any sharp peak else a wide hump near 28º, the plot indicate that it is a glassy material.

Absorption Spectra (upc)

Figure 3 displays the absorption spectra of the TNZTY glass doped with Tb-Yb ions. For the 0.5% Yb^{3+} and 0.5% Tb^{3+} -0.5% Yb^{3+} codopants, a significant absorption band centred at 978 nm is visible as a result of the Yb^{3+} transition from ground state $^2F_{7/2}$ to excited state $^2F_{5/2}$. The absorption

peaks from the Tb^{3+} transitions are located at 486 nm ($^7F_6/^5D_4$) in the Tb^{3+} single doped glass. The overlapping absorption bands are believed to be the result of the transition from $^5D_0$ to $^3H_7$ excited-state levels, which occurs in the visible-ultraviolet area between 300 and 430 nm. It is challenging to properly assign and breakdown them, though.

The comparatively strong absorption bands seen between 320 and 500 nm suggest that the codopants could be readily accessible for the absorption of high energy photons.

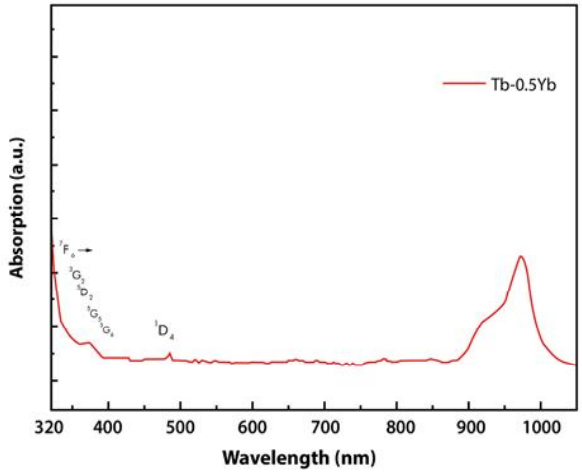

Fig. Absorption spectra of TNZTY glass

Upconversion Spectra UC :

The upconversion spectra of TNZTY glass doped with Tb-Yb ions under 978nm laser irradiation are shown in Fig. 4. It is evident that there are distinct, strong emission peaks with energy upconversion ranging from 350 to 700 nm, which are related to the Tb^{3+} transitions ^{5}D4-^{7}F6 (492 nm), $^5D_4$-$^7F_5$ (^{5}42 nm), $^5D_4$-$^7F_4$ (581 nm), and $^5D_4$-$^7F_3$ (622 nm)[17].

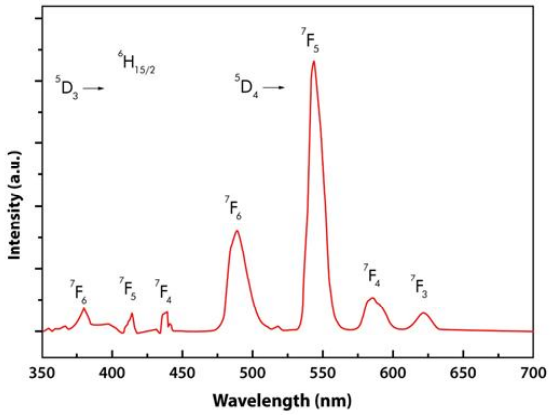

Fig. 4, Emission spectra of TNZTY glass at 978nm excitation

Furthermore, emissions corresponding to the $^5D_3$-$^7F_6$, $^5D_3$-$^7F_5$, and $^5D_3$-$^7F_4$ transitions, which are situated in the 370–450 nm range, have been identified. Tellurite glasses are known to have lower phonon energy than borate or silicate glasses. Additionally, the non-radiative transition rate of lanthanide ions decreases with the maximal phonon energy of the host matrix. It is possible to observe the upconversion luminescence, which is a sign that co-doped glass experiences an efficient energy transfer (ET) from Yb^{3+} to Tb^{3+}. The distance between Tb^{3+} and Yb^{3+} ions becomes shorter as a result of their incorporation into the glass matrix than it would be if these ions were uniformly distributed in precursor glass. This will increase the energy transfer efficiency and further improve the upconversion luminescence.

Effect of Pump Power :

The intensity of upconversion I of these shifts was monitored as a function of the pump power P to get insight into the upconversion mechanisms. I is related to the nth power of P in the upconversion process, or $I \infty P^n$, where n is the amount of pump photons received for every upconverted photon released[12]. A straight line with slope n is produced when log I is plotted against log P. Figure 5 illustrates the power dependence of the upconverted intensity of TNZTY glass. The linear fitted gradients for emission values at 492 nm ($^5D_4$-$^7F_6$), 542 nm ($^5D_4$-$^7F_5$), 581 nm ($^5D_4$-$^7F_4$), and 622 nm ($^5D_4$-$^7F_3$), respectively, are 1.90, 1.74, 1.96, and 1.88. These findings show that in order to fill the $^5D_4$ emission level, two photons are needed.

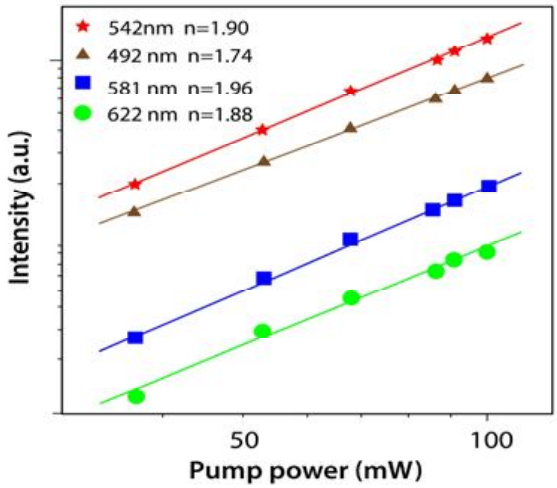

Fig. 5. Dependence of upconversion intensity on the pump power on TNZTY Glass.

These findings show that in order to fill the $^5D_4$ emission level, two photons are needed. Figure 6 analyzes and illustrates the upconversion mechanism in prepared glass based on the energy level diagrams of Tb^{3+} [17] and Yb^{3+}. Yb^{3+} ions in the ground $^2F_{7/2}$ state are populated to the excited $^2F_{5/2}$ state under 978 nm laser stimulation. Additionally, cooperative energy transfer (CET) from two Yb^{3+} ions in the $^2F_{5/2}$ state can evacuate one Tb^{3+} ion in the ground $^7F_6$ state to the $^5D_4$ excited state [8]. The following is a description of this CET process: $^2F_{5/2}$ (Yb^{3+}) + $^2F_{5/2}$ (Yb^{3+}) + $^7F_6$ (Tb^{3+}) - $^2F_{7/2}$ (Yb^{3+}) + $^2F_{7/2}$ (Yb^{3+}) + $^5D_4$ (Tb^{3+}). Green upconversion emissions are then produced by the radiative

relaxation of Tb^{3+} ions in $^5D_4$ level to $^7F_{3-6}$ levels. For upconversion from the $^5D_3$ level, a three-photon process rather than a two-photon process should be taken into account. The explanation is as follows. A third photon mechanism, namely excited state absorption (ESA) and/or ET from the third Yb^{3+} ion, could also excite Tb^{3+} ions in the $^5D_4$ level to the $^5D_1$ level. The $^5D_3$-$^7F_{4-6}$ emissions are then produced when Tb^{3+} ions in the $^5D_1$ level relax nonradiatively to the $^5D_3$ level.

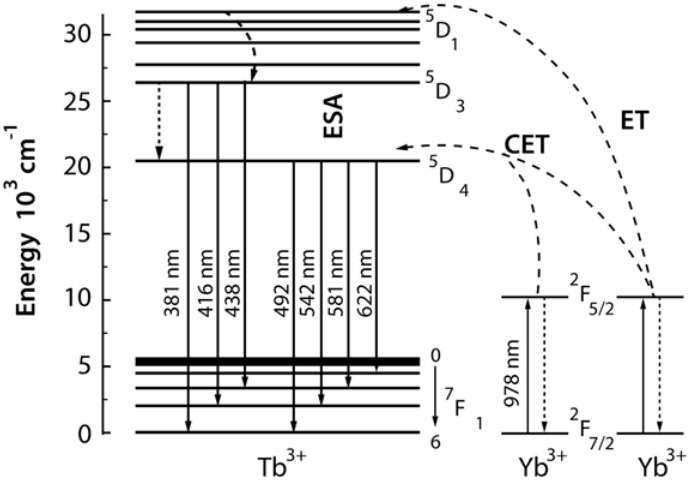

Fig. 6. Energy level diagrams of Tb^{3+} and Yb^{3+} and the possible upconversion mechanisms under 978nm excitation.

Conclusion

Using the traditional melt and quench process, Tb^{3+}–Yb^{3+} co-doped zinc tellurite glass with exceptional transparency was effectively manufactured. Both DSC and XRD have been used in the structural and thermal analyses. Precursor glass showed characteristic Tb^{3+} emissions from $^5D_4$-$^7F_{3-6}$ and $^5D_3$-$^7F_{4-6}$ transitions upon excitation with a 978 nm laser. The green emission was found to be caused by a two-photon mechanism that involved cooperative energy transfer from two Yb^{3+} ions to one Tb^{3+} ion, as confirmed by the laser power dependency of upconversion.

Abbreviations

DSC- Differential Scanning Calorimetry

XRD - X-ray differection

ET- Energy-Transfer

CET - Cooperative energy transfer

ESA - Excited state absorption

UV-VIS-IR- Ultraviolet-Visible-Infrared

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Conflicts of Interest

The authors declare no conflicts of interest.

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