



Intense red upconversion emission of Yb/Tm/Ho triply-doped tellurite glasses

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Abstract

YTH doped bismuth boro-tellurite glass (68%TeO₂-10%Bi₂O₃-20%B₂O₃-1%Yb₂O₃-0.5Tm₂O₃-0.5%Ho₂O₃) was created using traditional melt-quench techniques. The intense red upconversion emission at 660 nm (Red, Ho: ⁵F₅→⁵I₈) and lack of the typically observed 485 nm emission (Blue, Tm: ¹G₄→³H₆) were found to be caused by the direct sensitising effects of Yb ions (Yb→Ho) and indirect sensitising and self-depopulating effects of Tm ions (Yb→Tm→Ho). As TBBYTH-glass exhibits the maximum emission intensity at 660 nm, it is considered to be a potential active bismuth boro-tellurite glass for the development of red fibre lasers.

Keywords: bismuth boro-tellurite, melt-quench methods, upconversion.

5.1. Introduction

Due to its propensity to create Red-Green-Blue luminescence when excited by a 980 nm laser, Yb³⁺, Tm³⁺, and Ho³⁺ doped glasses have recently been the subject of several studies [1-3]. An alternative method to create suitable visible laser sources is to dope tellurite base glass with YTH. These sources can be used for advanced scientific instrumentation, bioscience gene sorting, underwater surveillance, and communications. They can also be used to create all-solid three-dimensional (3D) Red-Green-Blue displays and colorful laser projections. As an illustration, consider the uses in medical diagnosis and treatment: blue and green lasers are utilised for cancer detection and localisation, whereas red lasers may be employed on cancer cells, causing immediate cell death and tissue necrosis [4].

Rare earth (RE) ions-doped upconversion fibre lasers have certain clear benefits over other visible laser production techniques, such as second- and third-harmonic generation in nonlinear crystals. They deliver an excellent, diffraction-limited beam appropriate with up-to-date silica-based optical communication systems, and are reasonably inexpensive, compact, and simple to install. They are also length-controllable, self-cooling at a low power level, have a small beam waist with a radius of micrometre level, and are length-controllable [5]. The development of effective visual fibre lasers using RE ions-doped materials favours hosts with low phonon energies.

It has been established that tellurite glasses, which are oxide glasses, have the lowest phonon energy (700 cm⁻¹) overall oxide glasses, comprising borate (1400 cm⁻¹), phosphate (1200 cm⁻¹), silicate (1100 cm⁻¹), and germinate (900 cm⁻¹) glasses.

In this work, we describe the production and characterisation of a bismuth boro tellurite doped with Yb³⁺, Tm³⁺, and Ho³⁺. The bismuth boro tellurite glass with the formula (68%TeO₂-10%Bi₂O₃-20%B₂O₃-1%Yb₂O₃-0.5Tm₂O₃-0.5%Ho₂O₃) exhibits the highest red light intensity without introducing concentration-quenching phenomenon, making it particularly suitable for the development of red fibre lasers.

5.2 Experiments

A transparent and stable boro-bismuth-tellurite glass composition of 70TeO₂-10Bi₂O₃-20B₂O₃(TBB) was chosen as the host material [6]. The claim that tellurite glass containing 1%Yb³⁺ may exhibit the greatest green light intensity without causing the concentration-quenching effect has been supported [5]. Therefore, 1%Yb₂O₃-0.5%Tm₂O₃-0.5%Ho₂O₃ (weight percent) were chosen into the host TBB glass to form (68%TeO₂-10%Bi₂O₃-20%B₂O₃-1%Yb₂O₃-0.5Tm₂O₃-0.5%Ho₂O₃) TBBYTH glass. The following are the fabrication techniques and details: Reagent chemical powders with a purity of over 99.7% were carefully measured and uniformly mixed in a glass bottle, and then melted in an alumina crucible at 950 °C for 75 minutes inside a muffle furnace. The viscous melt was subsequently poured onto a stainless steel mould (shaped like a pellet) at 280 °C, annealed there for three hours to remove internal stress, and then slowly cooled to room temperature.

At ambient temperature, all the optical measurements were made. A spectrophotometer (Research India model number RI2SA) was used to capture the materials' absorption spectra between 350 and 1200 nm. By stimulating the samples with a continuous-wave laser diode that had an estimated pump intensity of 1 W mm² at 980 nm and an average power of 1.3 W, the fluorescence spectra were produced.

5.3 Results and Discussion

5.3.1. Absorption Properties

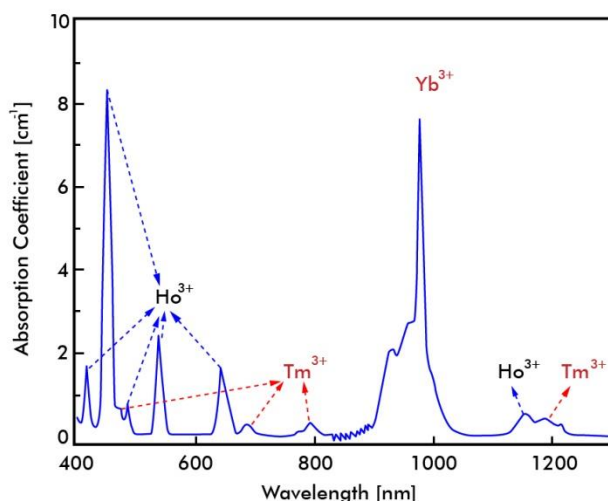


Fig.1, Absorption spectra of TBBYTH glass

Fig. 1 displays the absorption spectrum of TBBYTH glass. Ho^{3+} transition-related absorption bands include:

- (i) $^5\text{I}_8 \rightarrow ^5\text{G}_5$ at 418nm
- (ii) $^5\text{I}_8 \rightarrow ^5\text{G}_6$ at 450nm
- (iii) $^5\text{I}_8 \rightarrow ^3\text{K}_8$ at 478nm
- (iv) $^5\text{I}_8 \rightarrow ^5\text{F}_3$ at 485nm
- (v) $^5\text{I}_8 \rightarrow ^5\text{F}_3$ at 537nm
- (vi) $^5\text{I}_8 \rightarrow ^5\text{F}_5$ at 642 nm and
- (vii) $^5\text{I}_8 \rightarrow ^5\text{I}_7$ at 1164 nm .

The absorption bands belongs to Tm^{3+} transitions are observed as:

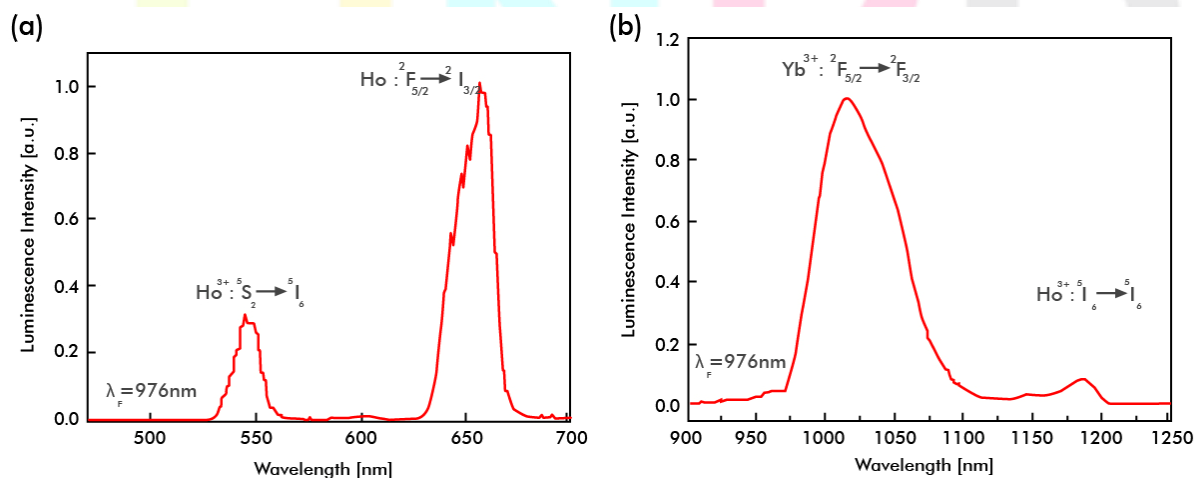
- (i) $^3\text{H}_6 \rightarrow ^1\text{G}_4$ bands at 466 nm,
- (ii) $^3\text{H}_6 \rightarrow ^1\text{G}_4$ at 688 nm,
- (iii) $^3\text{H}_6 \rightarrow ^3\text{F}_3$ at 794 nm, and
- (iv) $^3\text{H}_6 \rightarrow ^3\text{H}_4$ at 1200 nm.

Whereas Yb^{3+} consist only one prominent transition $^5\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ at 980 nm.

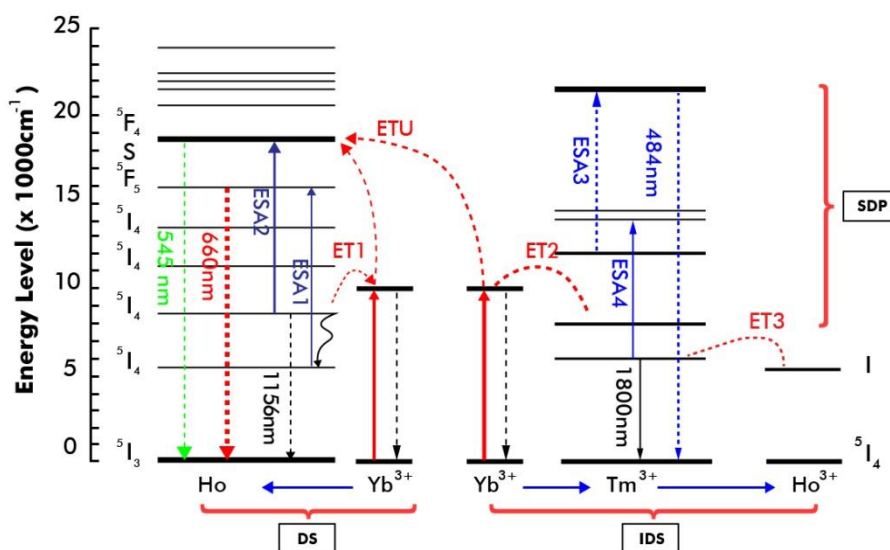
Due to the significant UV-edge absorption of the TBBYTH glass, the absorption bands in near VU range cannot be seen in the spectrum [5]. The glass samples exhibit high transparency in the visible range, suggesting that upconversion applications as visible fibre lasers may be feasible [7].

5.3.2. Emission Properties

The TBBYTH glass emits high upconversion luminescence in the visible area centred at 543 nm (Green, $\text{Ho}: ^5\text{S}_2 \rightarrow ^5\text{I}_8$) and 657 nm (Red, $\text{Ho}: ^5\text{F}_5 \rightarrow ^5\text{I}_8$), respectively, as illustrated in Fig. 2(a), under 980 nm excitation [3]. Due to differences in the local ligand field from site to site, the red and green emission bands are unevenly widened. The sample exhibits strong orange-yellow fluorescence, which is readily visible with the naked eye and can be interpreted as a mixture of red and green emissions with a specific ratio.



When pumped by a 980 nm diode laser, Ho^{3+} and Tm^{3+} ions cannot absorb the energy of excitation directly due to the lack of corresponding energy levels [1], but Yb^{3+} ions can absorb the NIR radiation efficiently and transfer the excitation energy to Ho^{3+} and Tm^{3+} as demonstrated in Fig. 3, including two direct sensitizing (DS) methods ($\text{Yb} \rightarrow \text{Ho}$; $\text{Yb} \rightarrow \text{Tm}$) and one indirect sensitizing (IDS) process ($\text{Yb}^{3+} \rightarrow \text{Tm}^{3+} \rightarrow \text{Ho}^{3+}$) [8]. We can infer that Tm ions act as an indirect sensitizing medium to transfer energy from Yb ions to Ho ions to improve the red emission of Ho ions but depopulate their blue emission at the cost; these effects, which are the first of their kind to be observed, are known as IDS and self-depopulating (SDP) effects of Tm ions. The lack of the typically observed 484 nm emission (Blue, Tm: ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$)



The collaborative energy transfer upconversion procedure, ETU, and two emission stimulated absorption procedures, ESA1 and ESA2, which present the observed red emission at 660 nm (Red, Ho: ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$) and the green one at 545 nm (Green, Ho: ${}^5\text{S}_2 \rightarrow {}^5\text{I}_8$), make the DS effects from Yb to Ho, Tm simple to understand. Therefore, we would want to pay greater attention to the recently discovered IDS and SDP impacts from Yb to Ho through Tm: $\text{Tm}^{3+} ({}^3\text{H}_5)$, $\text{Ho}^{3+} ({}^5\text{I}_6)$ and $\text{Yb}^{3+} ({}^2\text{F}_5)$ have similar energy levels, making it simple to transfer energy from Yb to Tm and Ho by direct ET1 and ET2 processes. Due to the narrow energy gap (600 cm⁻¹) between $\text{Tm} ({}^3\text{F}_4)$ and $\text{Ho} ({}^5\text{I}_7)$, as is stated [9], Tm can operate as the efficient medium to transfer the absorbed energy from Yb to Ho in the end; i.e., the IDS process connected with ET2 and ET3. The absence of the typically seen 484 nm emission (Blue, Tm: ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$), which might be considered an SDP procedure of Tm ions, was caused by the termination of two upconversion procedures, ESA 3 and ESA 4, as well as by this IDS procedure.

Conclusion

In conclusion, a collection of YTH triply-doped TBBYTH glass (68% TeO₂-10% Bi₂O₃-20% B₂O₃-1% Yb₂O₃-0.5Tm₂O₃-0.5% Ho₂O₃) was created and characterised with the goal of creating effective visible fibre lasers, particularly for the 660 nm red light fibre lasers. Due to the inclusion of Yb³⁺ and Tm³⁺ ions, the red upconversion

has been significantly improved in TBBYTH glasses. First, it is discovered that Tm³⁺ functions as a sensitising medium for the energy transfer from Yb³⁺ to Ho³⁺, which in turn causes Ho³⁺ to stop emitting blue light at 485 nm. Potential medical uses for TBBYTH glass-based fibre devices include the advancement of ultra-high resolution optical coherence tomography.

References

- [1]. B. Peng and T. Izumitani, "Blue, green and 0.8 μm Tm³⁺, Ho³⁺ doped up-conversion laser glasses, sensitized by Yb," *Opt. Mater. (Amsterdam)* 4, 701–711 (1995).
- [2]. X. Zou and H. Toratani, "Dynamics and mechanisms of up- conversion processes in Yb³⁺ sensitized Tm³⁺ and Ho³⁺ doped fluorozirconaluminate glass," *J. Non-Cryst. Solids* 181, 87–99 (1995).
- [3]. N. Q. Wang, X. Zhao, C. M. Li, E. Y. B. Pun, and H. Lin, "Up- conversion and color tunability in Tm³⁺/Ho³⁺/Yb³⁺ doped low phonon energy bismuth tellurite glasses," *J. Lumin.* 130, 1044–1047 (2010).
- [4]. D. L. Yang, H. Gong, E. Y. B. Pun, X. Zhao, and H. Lin, "Rare- earth ions doped heavy metal germanium tellurite glasses for fiber lighting in minimally invasive surgery," *Opt. Express* 18, 18997–19008 (2010).
- [5]. Z. Zhou, A. Lin, H. Guo, X. Liu, C. Hou, M. Lu, W. Wei, B. Peng, W. Zhao, and J. Toulouse, "Tb³⁺/Yb³⁺ heavily-doped tellurite glasses with efficient green light emission," *J. Non-Cryst. Solids* 356, 2896–2899 (2010).
- [6]. V. Bhingarkar, S. Bairagi, G. F. Materials Today: Proceedings, <https://doi.org/10.1016/j.matpr.2023.03.64>
- [7]. A. Lin, A. Rysanyanskiy, and J. Toulouse, "Fabrication and characterization of a water-free mid-infrared fluorotellurite glass," *Opt. Lett.* 36, 740–742 (2011).
- [8]. N. K. Giri, D. K. Rai, and S. B. Rai, "Multicolor upconversion emission from Tm³⁺ Ho³⁺ Yb³⁺ codoped tellurite glasses on NIR excitations," *Appl. Phys. B* 91, 437–441 (2008).
- [9]. Q. Y. Zhang, T. Li, and Z. H. Jiang, "980 nm laser-diode-excited intense blue upconversion in Tm³⁺/Yb³⁺-codoped gallate– bismuth–lead glasses," *Appl. Phys. Lett.* 87, 171911 (2005).