



Tb³⁺/Yb³⁺ co-doped Y₂O₃ upconversion transparent ceramics: Fabrication and characterization for IR excited green emission



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ABSTRACT

Tb³⁺/Yb³⁺ co-doped Y₂O₃ transparent ceramics were fabricated by vacuum sintering of the pellets (prepared from nanopowders by uniaxial pressing) at 1750 °C for 5 h. Zr⁴⁺ and La³⁺ ions were incorporated in Tb³⁺/Yb³⁺ co-doped Y₂O₃ nanoparticle to reduce the formation of pores which limits the transparency of ceramic. An optical transmittance of ~80% was achieved in ~450 to 2000 nm range for 1 mm thick pellet which is very close to the theoretical value by taking account of Fresnel's correction. High intensity luminescence peak at 543 nm (green) was observed in these transparent ceramics under 976 and 929 nm excitations due to Yb–Tb energy transfer upconversion.

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1. Introduction

The rare earth (RE) ion assisted upconversion has attracted much attention for their potential use in infrared (IR)-visible converters, short wavelength solid state lasers, high density optical storage, biological imaging, photonics and photovoltaics etc [1–3]. Among various co-doped RE ions (Tm/Yb, Er/Yb, Ho/Yb and Tb/Yb) investigated for upconversion the Tb/Yb co-doped materials have attracted attention due to green luminescence (~543 nm) from the ⁵D₄ – ⁷F₅ transition in Tb [4]. Although in most of the studies glasses have been used as host for Tb/Yb ions for fibre laser and amplifiers but the poor mechanical strength and poor heat resistance are drawbacks of glasses which limit their applications [4–10]. The increase in emission intensity of Tb/Yb doped glasses with increase in crystallinity has also been reported [5]. Therefore it is expected that the use of transparent ceramics or single crystal as host (high thermal conductivity and good heat resistance) will be suitable for high upconversion emission intensity.

Compared to single crystal, transparent ceramic hosts for RE ions are preferred because of some advantages like ease of fabrication, low temperature processing (which leads to undesirable wave front distortion), sustain high doping level, less expensive, engineering of

dopant layers for Q-switch applications etc. Moreover transparent ceramics can be manufactured in sizes limited only by the size of the processing equipment [11–13].

In this paper, we report the fabrication and photoluminescence studies of Tb/Yb codoped Y₂O₃ transparent ceramic which can be used directly as ceramic disk laser for green emission (i. e. without using any second harmonic non linear crystal). Moreover, the study on Tb/Yb codoped Y₂O₃ transparent ceramic, to the best of our knowledge, has not been previously reported. The Y₂O₃ was selected as host for Tb and Yb ions due to its high thermal conductivity (13.6 W/mK), high melting point (2430 °C), broad range of transparency (0.2–8 μm) and high corrosion resistance [10]. Additionally, it possesses relatively low phonon energy (~430–550 cm⁻¹) which would greatly increase the possibility of radiative transitions and in turn result in a high quantum yield of upconversion process.

2. Experimental

Aqueous solution (0.2 M) was prepared by dissolving Y₂O₃, Yb₂O₃, Tb₂O₃, La₂O₃ (purity 99.99%) and ZrOCl₂·8H₂O according to stoichiometry of (Tb_{0.01}Yb_{0.01}La_{0.01}Zr_{0.02}Y_{0.95})₂O₃ in dilute nitric acid. Precipitation was carried out by adding (1 M) ammonia solution at 10 ml/min. Ammonium Sulphate solution and methanol was used as surfactant and washing solvent respectively. The precipitate was separated by centrifugation and dried at 80 °C which was subsequently calcined at 900 °C to get desired oxide pow-

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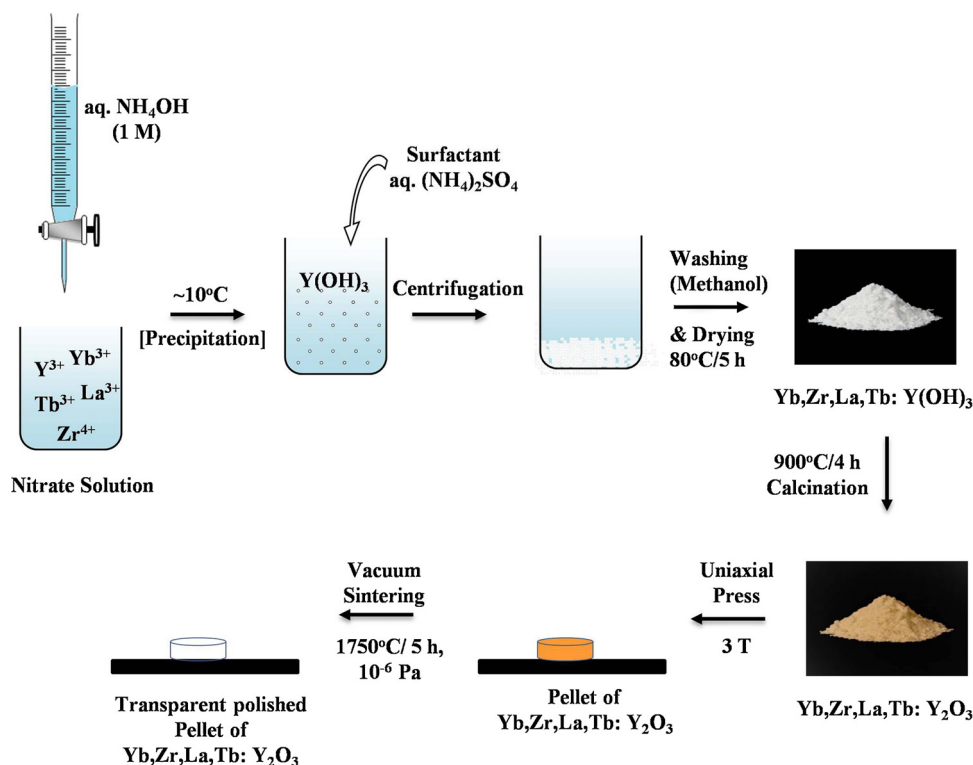


Fig. 1. Schematic details of synthesis of nano particles by co-precipitation method and fabrication of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ transparent ceramic.

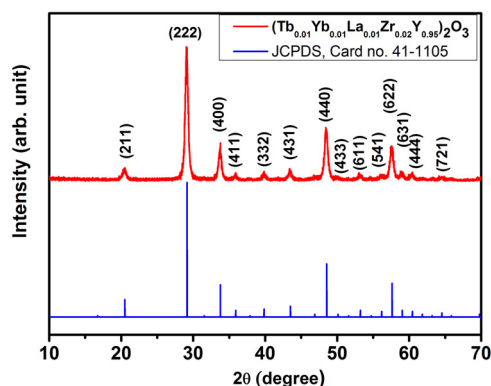


Fig. 2. X-ray diffraction pattern of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ nanopowder.

der. The calcined powder was uniaxially pressed and then sintered at 1750 °C for 5 h using high vacuum furnace to get transparent ceramic pellet. Finally the pellets were double-side polished to 1 mm thickness. The schematic details of synthesis of nano particles and fabrication of transparent ceramic pellet is shown in Fig. 1. The nano particles were characterized using Rigaku X-ray diffractometer, Zetasizer Nano ZS90 nanoparticle analyzer, Zeiss field emission scanning microscope (FESEM) and Malvern Zetastar 90 (model no-ZEN 3690) particle size analyzer. The transparent ceramics were characterized using V-670 transmission spectrophotometer (JASCO Corporation) and FLS920-s fluorescence spectrometer (Edinburgh Instruments Ltd.).

3. Results and discussion

The XRD pattern of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ nanopowder (Fig. 2) confirms the formation of crystalline cubic Y_2O_3 single phase (JCPDS, Card no. 41-1105). The addition of dopants like Tb^{3+} , Yb^{3+} , Zr^{4+} and La^{3+} in the specified concentration does not lead to

any change in the phase of Y_2O_3 . In order to determine the structure, the diffraction pattern was Rietveld refined using Materials Studio program. The program allowed us to reproduce all observed reflections and gave all identical reliability factors. The profile fits for the Rietveld refinement of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ sample is shown in Fig. 3(a). We have illustrated structural parameters for $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ sample and also identified the residual for the weighted pattern R_{wp} (4.51%) and the pattern R_p (11.12%). It is noticed that the observed and calculated pattern are in good agreement with no trace of phase transition from cubic to any other crystal structure due to addition of dopants. The XRD pattern of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ was refined with cubic $Im-3$ space group and obtained refined lattice parameters are $a=b=c \sim 10.6141 \text{ \AA}$. The volume and density of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ are found to be 1195.7753 \AA^3 and 5.0175 g/cm^3 respectively.

The refined crystal structure of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ is shown in Fig. 3(b). The unit cell contains 16 formula units with 32 cations that form 24 sites of C_2 symmetry oriented parallel to $\langle 100 \rangle$ and 8 sites of C_{3i} symmetry, with threefold along $\langle 111 \rangle$. From position coordinates it is found that dopants uniformly replaced Y^{3+} ions. In this structure cations occupies 8b special Wyckoff positions at (0.25, 0.25, and 0.25) and 24d Wyckoff positions at (0.9681, 0, 0.25) and oxygen occupies the 48e positions at (0.3932, 0.1532, 0.3819). The Y atoms are octahedrally (dark cyan) coordinated by O atoms (red) as shown in Fig. 3(b).

The FESEM micrograph of nanocrystallized $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ powder is shown in Fig. 4(a). The particles were well separated and have spherical morphology with size in $\sim 20\text{--}50 \text{ nm}$ range. Fig. 4(b) shows particle size distribution of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ nanopowder measured by dynamic light scattering method. The size distribution of nanoparticles was found to be in $15\text{--}90 \text{ nm}$ range with most of particles are in the range of $15\text{--}40 \text{ nm}$, which has an added advantage in fabrica-

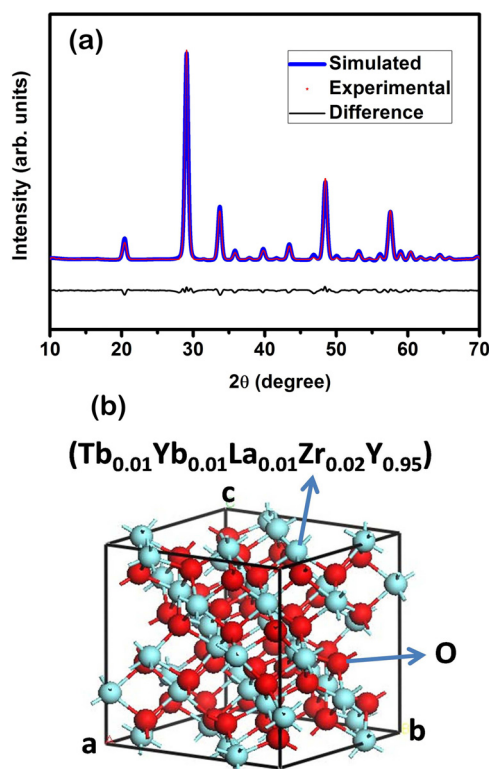


Fig. 3. (a) Reitveld refined X-ray diffraction patterns of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$. (b) Refined cubic crystal structure of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

tion of transparent ceramic as it avoids the problem of differential sintering.

A flat transmittance of $\sim 80\%$ has been observed (in ~ 450 to ~ 2000 nm range) in transmittance spectrum of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ ceramic pellet (Fig. 5) which is comparable to theoretical transmittance ($\sim 83\%$) of Y_2O_3 . The absorption band between 888 and 996 nm (maximum peaks at 976 and 906 nm) in the transmission spectrum arises due to transition between $^2\text{F}_{7/2}$ to $^2\text{F}_{5/2}$ states of Yb^{3+} ion. From UV cut off (at ~ 309 nm i.e. at $2/3$ of maximum intensity) of transmission spectrum, bandgap of the sample was calculated to be 4.01 eV which is comparable to theoretical bandgap of Y_2O_3 i.e. 4.54 eV [14]. Inset of Fig. 4 shows the image of fabricated $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ transparent ceramic.

The excitation spectrum of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ transparent ceramic was recorded by keeping the emission detector fixed at 543 nm (Fig. 6(a)). A band (~ 880 to ~ 990 nm) with high intensity peaks at 891, 902, 911, 929, 943, 961 and 985 nm were observed in excitation spectrum. This also showed that highest emission intensity (at 543 nm) will be observed at 929 nm excitation. However, the transmission spectrum shows high absorption intensity at 976 nm. Thus upconverted emission spectra were recorded for 929 nm (highest intensity peak wavelength in excitation spectrum (Fig. 6(a))) and 976 nm (highest absorption peak in transmission spectrum (Fig. 5)) excitation as shown in Fig. 6(b). Since Tb^{3+} ions do not absorb the incident IR (929 and 976 nm) radiation, its excitation is dependent on energy transfer from excited Yb^{3+} ions. The emission spectra for both excitations (929 and 976 nm) are identical except emission intensity which is higher for 929 nm excitation. The PL intensity at 543 nm emission is high (10^5 counts per second with 0.5 excitation and emission band width) for 929 and 976 nm excitation. The Tb^{3+} emission includes band at ~ 483 nm, ~ 543 nm (green strongest), ~ 583 nm and ~ 625 nm involving the electronic transi-

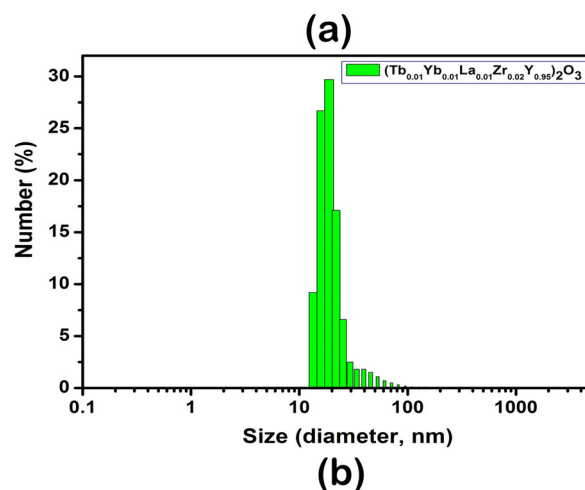
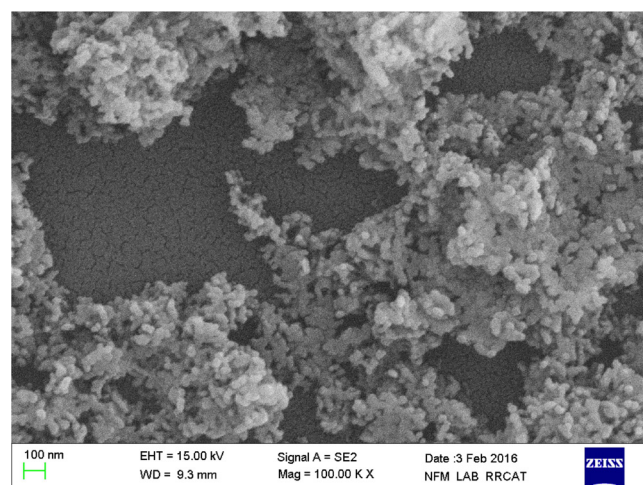


Fig. 4. (a) FESEM image of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ nanoparticles. (b) Particle size distribution of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ nanoparticles.

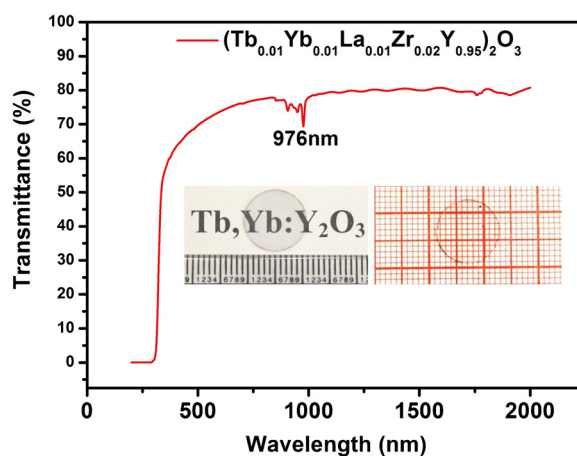


Fig. 5. The optical transmission spectra of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ sintered pallet. The inset shows the Photograph of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ sintered pallet of thickness 1 mm.

tions $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ respectively. The Tb^{3+} ions in the $^5\text{D}_4$ level may further absorb a 929/976 nm photon or receive excitation transfer from an excited Yb^{3+} ($^2\text{F}_{5/2}$) ion, raising the Tb^{3+} ions to the $^5\text{D}_1$ level which decays non-radiatively to $^5\text{D}_3$ and $^5\text{D}_4$ levels adding to the above mentioned transitions. However, the radiative emission from $^5\text{D}_3$ level was not recorded

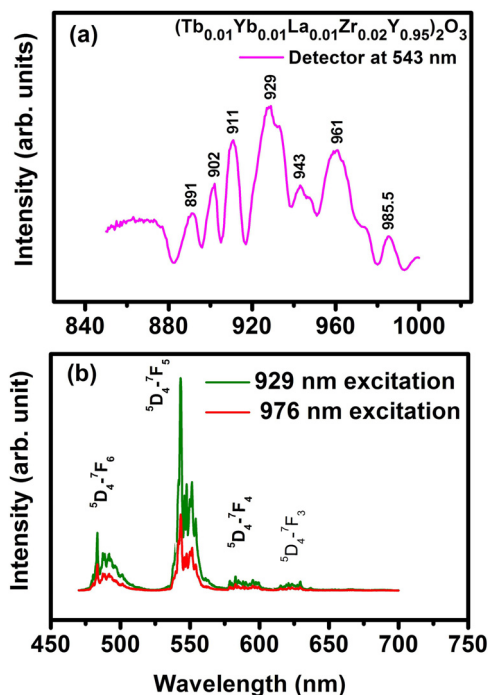


Fig. 6. (a) Excited spectrum of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ transparent pellet by keeping detector at upconverted frequency i.e. at 543 nm. (b) Upconverted emission spectra of $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ transparent pellet excited at 929 and 976 nm.

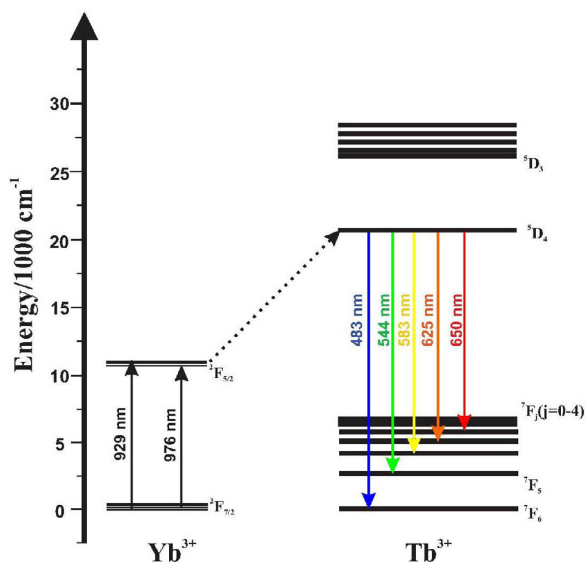


Fig. 7. Possible energy level diagram of Yb^{3+} and Tb^{3+} and mechanism for frequency upconversion and energy transfer from Yb^{3+} to Tb^{3+} .

in PL spectra due to its confined range kept to avoid unwanted diffraction peaks from diffraction grating. Similarly the peak due to cooperative luminescence process is also avoided which could be observed at ~ 453 nm [5].

It is also seen from the energy level diagram for Yb^{3+} and Tb^{3+} ions (Fig. 7) that no direct transfer of excitation energy from an Yb^{3+} ion in $^2F_{5/2}$ level is possible. Thus one has to consider the energy transfer simultaneously from a pair of Yb^{3+} ions both excited to the $^2F_{5/2}$ level and this process is termed as cooperative sensitization. This excitation populates 5D_4 level of the Tb^{3+} ion and results in a strong green emission.

4. Conclusions

Nanopowders of Tb^{3+} , $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ were prepared by coprecipitation method. Transparent ceramic pellets (prepared by uniaxial pressing of nanopowders) were fabricated successfully by vacuum sintering at 1750°C for 5 h. Zr^{4+} and La^{3+} utilized as sintering additive, which controls random grain growth during sintering, were incorporated in the nanoparticle during synthesis. Transmittance of $\sim 80\%$ was achieved in 1 mm thick pellet (in ~ 450 to ~ 2000 nm range). Upconverted emission peaks at ~ 483 , ~ 543 , ~ 583 and ~ 625 nm were observed for IR excitation at 929 and 976 nm. The strong emission band observed at 543 nm with high PL intensity due to Yb-Tb energy transfer upconversion indicates that $(\text{Tb}_{0.01}\text{Yb}_{0.01}\text{La}_{0.01}\text{Zr}_{0.02}\text{Y}_{0.95})_2\text{O}_3$ transparent ceramic is a promising gain medium for the generation of green laser.

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