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# White light emission in $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped $Y_2O_3$ transparent ceramic

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ABSTRACT

$Tm^{3+}/Er^{3+}/Yb^{3+}$ triply doped $Y_2O_3$ transparent ceramics were fabricated by solid state reaction and characterized from the point of view of white light upconversion luminescence. All the samples exhibited high transparency not only in near-infrared band but also in visible region. Strong red ($Er^{3+}$: $^4F_{9/2} \rightarrow {}^4I_{15/2}$), green ($Er^{3+}$: $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$) and blue ($Tm^{3+}$: $^1G_4 \rightarrow {}^3H_6$) upconversion emissions have been observed under 980 nm excitation at room temperature. By varying the concentration of $Er^{3+}$ ion, various colors of upconversion luminescence (pure blue, bluish green, pure green and yellowish green), including white light with CIE-$X$ = 0.295 and CIE-$Y$ = 0.312, can be easily achieved.



## 1. Introduction

In recent years, there has been great interest in the generation of white light for large-area applications such as light-emitting diode (LED), electroluminescence device, back light and liquid-crystal display (LCD). One of the effective ways for generating white light is rare earth (RE) ions doped material based on frequency upconversion process, which can convert near-infrared photons into visible photons via multiphoton processes [1–6]. Downing et al. reported simultaneous generation of RGB fluorescence in $Tm^{3+} + Er^{3+} + Pr^{3+}$ triply doped fluoride glasses [7]. Dwivedi et al. reported white upconversion emission in Pr/Er/Yb codoped tellurite glass [8], and Giri et al. obtained white light in Tm/Ho/Yb codoped tellurite and germanate glasses [9]. White color emission was also realized in various other combinations of RE ions, such as Eu/Mn [10], Dy/Ce [11] and Eu/Tb/Ce [12]. Recently, researchers have realized white light emission in nano structure, such as nanorod [13] and nano particles [14].

However, as the host materials are limited to glass, film and phosphor, the applications are greatly restricted due to the poor chemical stability and low damage threshold of the hosts [15]. Transparent ceramic materials have caused great concern to the researchers since the first laser demonstration on Nd:YAG ceramic in 1995 [16], but reports about the white light emission in transparent ceramics are quite a few. Compared with the host materials mentioned above, transparent ceramic can be highly transparent in the ultraviolet–visible–infrared range, which is benefit for the output of the upconversion luminescence. Above all, transparent ceramic exhibits good physical, chemical, mechanical and ultraviolet radio-resistance stability [17], which assures that they can be used in devices (such as laser and sensor) more conveniently. Among them, $Y_2O_3$ transparent ceramic has received great attention for its potential application in IR windows, domes and lasers due to its chemical durability and high thermal conductivity [18,19]. Most importantly, it possesses relatively low phonon energy (~430–550 $cm^{-1}$) which makes it possible to obtain high upconversion luminescence efficiency. In this letter Tm/Er/Yb codoped $Y_2O_3$ transparent ceramics were fabricated by solid-state reaction, and the upconversion luminescence was characterized, aimed to use it as potential host material for white light emission.

## 2. Experiment

High purity (99.999%) $Y_2O_3$, $Yb_2O_3$, $Tm_2O_3$ and $Er_2O_3$ were used as starting materials with 3.0 at.% $ZrO_2$ as additive [20]. The concentration of $Tm^{3+}$ and $Yb^{3+}$ ions was fixed at 0.1 at.% and 3.0 at.%, respectively, while the concentration of $Er^{3+}$ ion varies from 0 to 2.0 at.%. According to the designed composition $(Er_xTm_{0.001}Yb_{0.03}Zr_{0.03}Y_{0.939-x})_2O_3$ ($x$ = 0(S0), 0.001(S1), 0.005(S2), 0.01(S3), 0.02(S4)), the powders were blended and ball milled in absolute ethylalcohol for 24 h with agate balls. After drying at 130 °C for 24 h, the powders were first uniaxially pressed into plates with 20 mm in diameter at 10 MPa and then cold isostatically pressed at 200 MPa. Transparent ceramics were obtained after sintering at 1800 °C under a base pressure of ~$1.0 \times 10^{-3}$ Pa for 20 h.

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**Fig. 1.** Photographs of Tm/Er/Yb codoped $Y_2O_3$ transparent ceramic.

The specimens were double-side polished to 1.0 mm thick to measure the optical transmittance spectra on a V-570-type ultraviolet/visible/near-IR spectrophotometer (JASCO, Japan). JSM 6360-LA scanning electron microscope (SEM) was used to analyses the microstructures of the polished surface after being etched in $H_3PO_4$ for 3 min at 85 °C. The up-conversion luminescence spectra were obtained with a TRIAX550 spectrofluorimeter with resolution of 0.5 nm upon the excitation of 980 nm laser diode (LD). In order to compare the upconversion spectra and colors, all the samples were kept under the same excitation condition during the optical measurement, and all the characterizations were performed at room temperature.

## 3. Results and discussion

Fig. 1 shows the photographs of Tm/Er/Yb codoped $Y_2O_3$ transparent ceramics. Each pellet is ~15 mm in diameter and ~1.0 mm thick. All the samples have relatively high transparency and the letters under the ceramics can be seen distinctly. The pink color deepens with the increasing of $Er^{3+}$ ion content.

XRD $\theta$–$2\theta$ scan of Tm/Er/Yb codoped $Y_2O_3$ transparent ceramics is presented in Fig. 2(a). It was observed that the addition of the RE ions hardly changes the phase structure of the ceramics. All the samples were well crystallized and coincided with cubic $Y_2O_3$ phase (JCPDS 41-1105). As presented in Fig. 2(b), the microstructure of the sintered ceramics (S2 chosen as sample) is comparatively homogeneous without abnormal grain growth, and the grain boundary is clear without any pores or impurities.

The optical transmittance curves of the transparent ceramics are shown in Fig. 3(a). The high transmittance in the visible region ensures the output of upconversion luminescence. The difference in transmittance between these samples might attribute to different sintering and polishing conditions, and the transmittance could be further enhanced with an optimal transparent ceramic preparing process such as slip casting or hot isostatic pressing sintering. The refined absorption spectrum in the 300–1800 nm region of S2 is presented in Fig. 3(b). The absorption peaks located at 942, 970 and 1025 nm are attributed to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition $Yb^{3+}$ ion. The absorption bands centered at 398, 684, 1200 and 1632 nm are assigned to the transitions of $Tm^{3+}$ ion from the ground state $^3H_6$ to the excited states $^1G_4$, $^3F_3$, $^3H_5$ and $^3F_4$, respectively [21]. Three absorption peaks, at 380, 522 and 1528 nm are attributed to $Er^{3+}$ ion, corresponding to the transitions from the ground state $^4I_{15/2}$ to the excited states $^4G_{11/2}$, $^2H_{11/2}$ and $^4I_{13/2}$, respectively.

Fig. 4 gives the up-conversion luminescence spectra upon excitation of 980 nm laser diode (LD) with 145 mW. The emission bands centered at 546, 558 nm (green) and 656 nm (red) are attributed to the transitions from excited states $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ to the ground state $^4I_{15/2}$ of $Er^{3+}$ ion, respectively. The intense blue emission centered at 480 nm is attributed to $Tm^{3+}$ ion, corresponding to the $^1G_4 \rightarrow {}^3H_6$ transition. Besides the blue emission, considerably intense violet emission at 360 nm and weak red emission at 650 nm were also detected, which are ascribed to $^1D_2 \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3F_4$ transitions of $Tm^{3+}$ ion. It is important to point out that the up-conversion luminescence at 360 nm of $Tm^{3+}$ ion can only be observed in low-phonon materials such as fluoride and oxyfluoride. $Y_2O_3$ is the only oxide in which ultraviolet upconversion fluorescence is detected [22]. This is mainly attributed to its low phonon energy, which can decrease the nonradiative loss due to multiphonon relaxation.

In up-conversion, the emission intensity $I_{up}$ is proportional to the $n$th power of the pump power as $I_{up} \propto P_{pump}^n$, where $n$ is the number of infrared photons required to absorb for emitting one visible photon. A plot of logarithm $I_{up}$ versus logarithm $P_{pump}$ yields a straight line with slope $n$, as shown in Fig. 5. The values of $n$ for green (546 and 558 nm) and red (656 nm) emissions approach 2, indicating that a two-photon process is involved to populate the $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ levels through energy transfer (ET) from $Yb^{3+}$ to $Er^{3+}$ ion. For $Tm^{3+}$ ion, The values of $n$ for blue (480 nm) and red (650 nm) emissions approach 3, indicating that the population of $^1G_4$ is accomplished by the three-step sequential energy transfer from the same excited $Yb^{3+}$ to $Tm^{3+}$ ion. The dependence of intensity at 360 nm on pump power could not be measured because of weak emission. But the $^1D_2$ state cannot be populated by a four-photon process via ET from $Yb^{3+}$ to $Tm^{3+}$ ion because of the large energy mismatch between $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of $Yb^{3+}$ ion and $^1G_4 \rightarrow {}^1D_2$

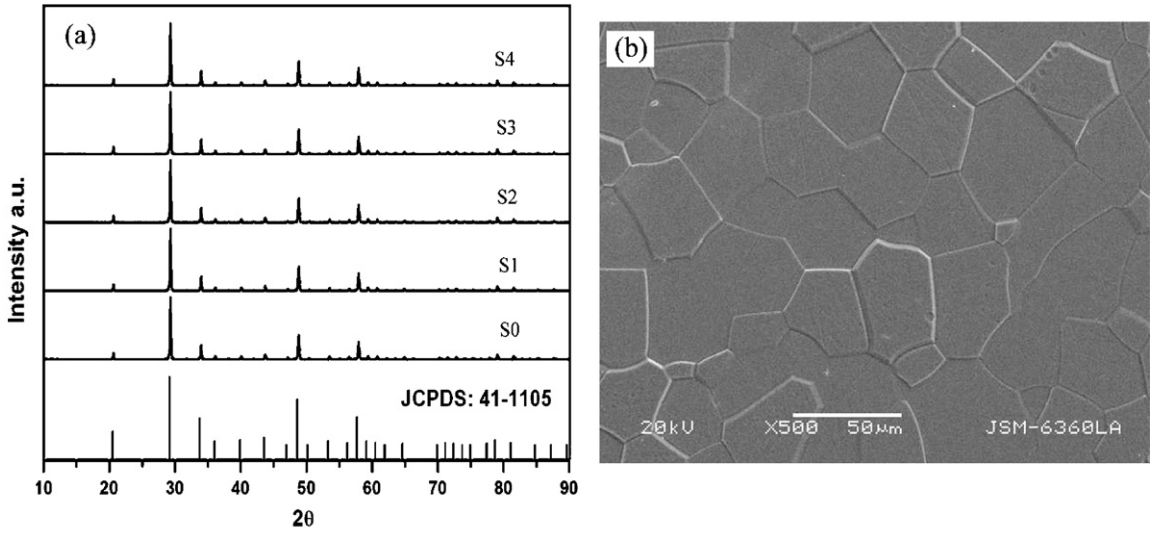


**Fig. 2.** (a) XRD patterns of Tm/Er/Yb codoped $Y_2O_3$ transparent ceramics. (b) SEM image of S2.

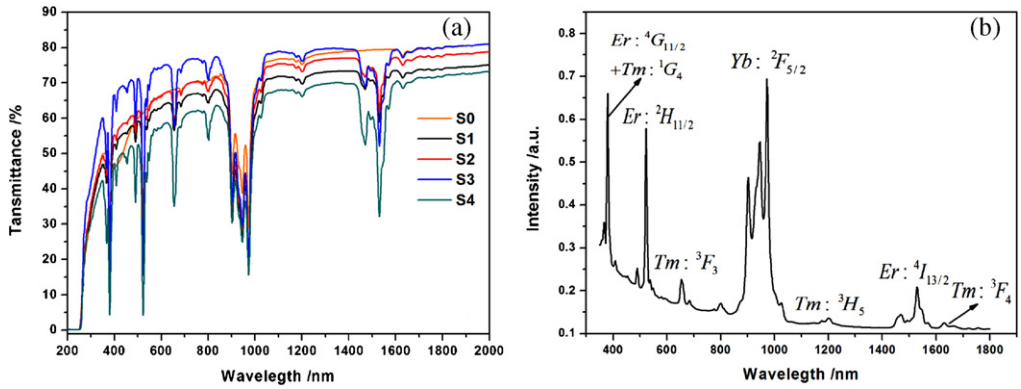


**Fig. 3.** (a) Optical transmittance of Tm/Er/Yb codoped $Y_2O_3$ transparent ceramic. (b) Optical absorption spectrum of S2.

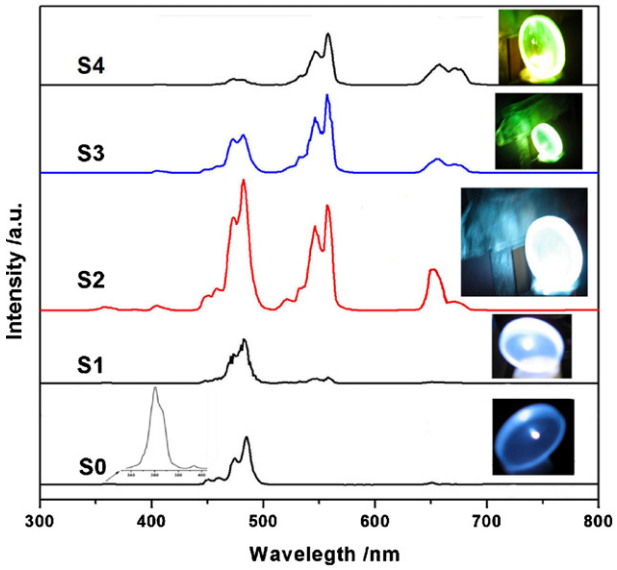


**Fig. 4.** Upconversion luminescence and apparent color of the transparent ceramics.

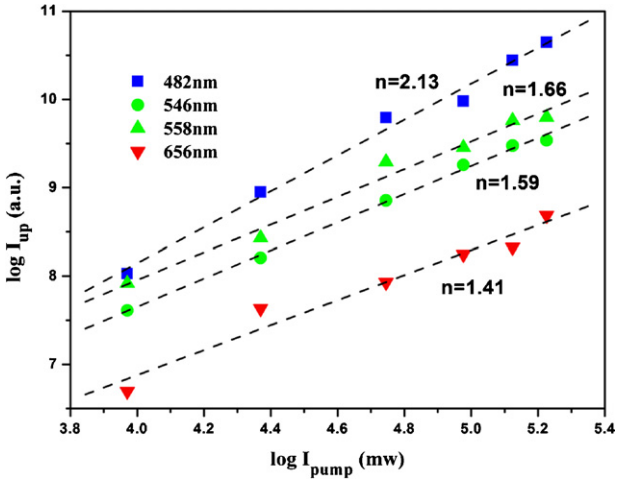


**Fig. 5.** Plots of logarithm $I_{up}$ versus logarithm $P_{pump}$ of emissions at 482, 546, 558 and 656nm.

of $Tm^{3+}$ ion (about 3500 $cm^{-1}$). The cross relaxation process of $^3F_{2,3} + {}^3H_4 \rightarrow {}^1D_2 + {}^3H_6$ between $Tm^{3+}$ ions plays an important role in populating $^1D_2$ level [23]. It is also observed that the intensity of blue luminescence is weakened with the increasing of $Er^{3+}$ ion concentration, which is attributed to the depopulation of $^3H_4$ excited level of $Tm^{3+}$ ion by the near resonant energy transfer from $Tm^{3+}$ to $Er^{3+}$ ion, i.e., $^4I_{15/2}(Er^{3+}) + {}^3H_4(Tm^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}) + {}^3F_4(Tm^{3+})$, $^4I_{15/2}(Er^{3+}) + {}^3H_4(Tm^{3+}) \rightarrow {}^4I_{9/2}(Er^{3+}) + {}^3H_6(Tm^{3+})$ [24]. The proposed upconversion mechanism for $Yb^{3+}$ ion sensitized $Tm^{3+}$ and $Er^{3+}$ ions in $Y_2O_3$ transparent ceramic are demonstrated in Fig. 6 in detail.

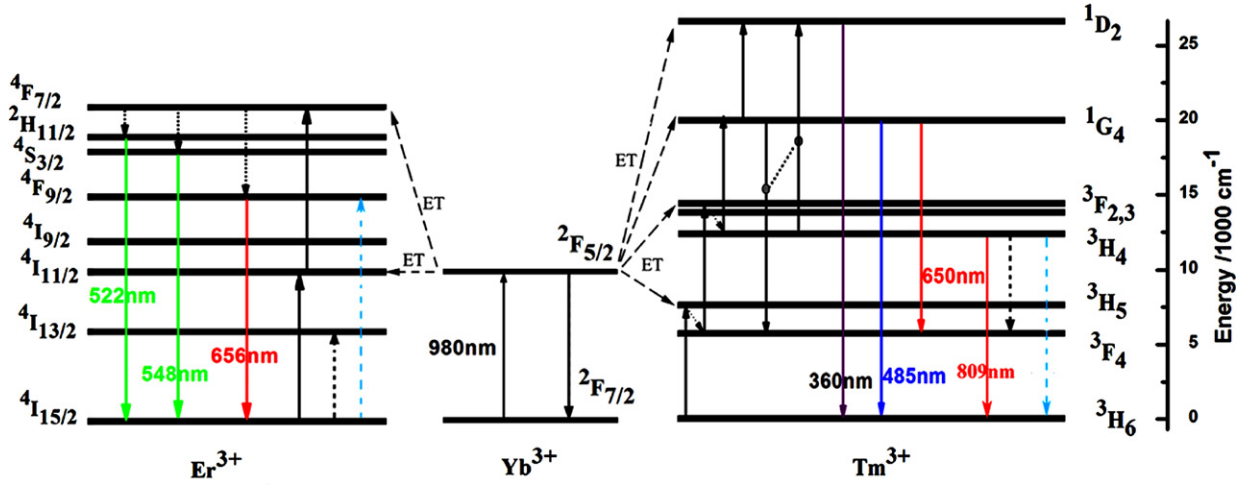


**Fig. 6.** Schematic energy level diagrams as well as the proposed up-conversion mechanism under 980 nm excitation. Dot lines indicate the energy transfers between $Tm^{3+}$ and $Er^{3+}$ ions.

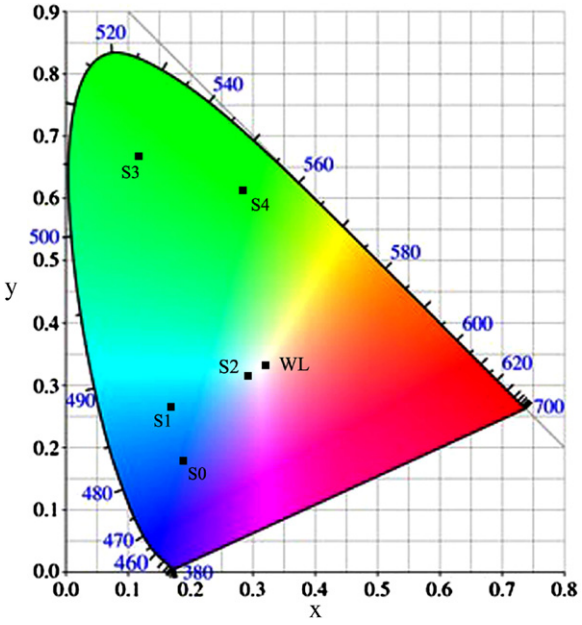


**Fig. 7.** CIE(*X*,*Y*) coordinate diagram showing the chromaticity points of the upconversion luminescence in $Y_2O_3$ transparent ceramic.

The emission spectra exhibit great changes depending on $Er^{3+}$ ion content. When the concentration of $Er^{3+}$ ion is low, the dominate emission is around 480 nm (blue). With the increasing of $Er^{3+}$ ion content, the color of luminescence change from blue to green, and then to yellowish green. It is worthy to note that in the upconversion emission spectra of S2, three emission bands at 480 nm (blue), 548 nm (green) and 656 nm (red) are observed with almost equal intensity, which results in the occurrence of white light. And the white light emission is strong enough to illuminate surrounding equipment. Although, the apparent luminescence of S2 presents a bluish tinge in the vision, it is quite close to the white light and can be improved further by optimizing the concentration of the rare-earth ions.

The upconversion emission spectra for the samples with different $Er^{3+}$ ion contents can be converted to the CIE 1931 chromaticity diagram and plotted in Fig. 7. For the Tm/Er/Yb triply doped $Y_2O_3$ transparent ceramic, the apparent luminescence can be tuned to pure blue ($X = 0.201$, $Y = 0.173$), bluish green ($X = 0.158$, $Y = 0.265$), white ($X = 0.295$, $Y = 0.312$), pure green ($X = 0.132$, $Y = 0.682$) or yellowish green ($X = 0.285$, $Y = 0.616$) with the variation of $Er^{3+}$ content ($x = 0$, 0.001, 0.005, 0.01 or 0.02, respectively). The CIE coordinate of S2 is ($X = 0.295$, $Y = 0.312$), which is fairly close to the standard equal energy white light illuminate ($X = 0.333$, $Y = 0.333$, denoted as WL in Fig. 7).

## 4. Conclusions

Tm/Er/Yb triply doped $Y_2O_3$ transparent ceramics have been synthesized and characterized. Efficient green and red upconversion fluorescence of $Er^{3+}$ ion and strong blue upconversion emission of $Tm^{3+}$ ion have been observed under 980 nm excitation at room temperature. By varying the content of $Er^{3+}$ ion, the fluorescence color can be tuned from multicolor to white color. All the results indicate that $Y_2O_3$ transparent ceramic is a potential host material for white light emission, and realizing white light emission in transparent ceramic might have a broad application prospects.

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