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ORIGINAL PAPER

Upconversion Based Tunable White-Light Generation in Ln: Y_2O_3 Nanocrystalline Phosphor (Ln = Tm/Er/Yb)

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Abstract We report the generation of efficient white light based on upconversion (UC) in $Tm^{3+}/Er^{3+}/Yb^{3+}$: Y_2O_3 nanocrystalline phosphor synthesized by simple and cost effective solution combustion technique on 976 nm laser excitation. The calculated color coordinates (using 1931 CIE standard) for samples annealed at different temperatures vary from (0.16, 0.30) to (0.32, 0.33) with dopant concentration, annealing temperature and the pump power; thus providing a wide color tunability including the white one. White emission is observed even at a very low laser power (60 mW). The maximum upconversion efficiency obtained for white emission is 2.79% with the color coordinates (0.30, 0.32) at laser power of 420 mW which is quite close to the standard white color coordinates.

Keywords Y_2O_3 phosphor · Upconversion · White emission · CIE coordinates

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Introduction

It has been a matter of great interest to develop rare earth (RE) doped materials that can result in efficient white light generation using cost effective diode laser. One of the methods to produce white light is by mixing the light of red, green and blue (RGB) colors in proper proportion. RE ions give narrow width intense color emission through upconversion when pumped with NIR radiation. Thus by having two or three RE ions emitting these colors in proper proportion, it is possible to generate the white light. These materials have potential applications in various fields such as optical displays and are very good alternatives to general lighting appliances (incandescent light bulb) [1, 2]. White light generation has been reported in various host materials like glasses, ceramics [3, 4] but there are very few reports on yttrium based nanocrystalline phosphors particularly prepared by solution combustion technique. There are recent reports on Tm/Er/Yb system in which either glass or ceramics have been used as host to get white light emission [5–7]. However there is limited study on this system in phosphor host [8, 9]. In this context RE doped Y_2O_3 based phosphor materials have been of great scientific and technological interest because of their attractive physical, chemical and optical properties; low phonon frequency and high thermal stability [7].

Actually the RGB emission in this group of REs comes from Tm^{3+} and Er^{3+} ions. The emission efficiency of RE can be improved several times in the presence of sensitizers. Among the various sensitizers Yb^{3+} ion has been shown to be especially effective when NIR pumping is involved. There are several reports on the enhancement of emission intensity based on Yb^{3+} ions sensitization in

doubly or triply doped matrices [10–14]. It has its lowest excited state $^2F_{5/2}$ at $\Delta E \sim 10\ 323\ cm^{-1}$ (λ=976 nm) above its ground state, which avoids any undesirable absorption of the incident radiation. Since Tm and Er doped matrices are well known blue, green and red luminescent materials respectively when pumped with NIR radiation (976 nm), it is possible to make a white-light source based on these UC materials [15]. Such a white-light source has all the advantages of UC-based displays such as high brightness, high efficiency, and long lifetime. Indeed it is important to note that the low energy pump photons do not cause damage to these UC materials because the excitation source used is in the NIR region. Other efficient white-light sources based on down-conversion may not achieve such high brightness because the high energy pump photons may degrade the emitters [16].

In this article we report the generation of tunable white light from $Tm^{3+}/Er^{3+}/Yb^{3+}$: Y_2O_3 nanocrystalline phosphor through single laser excitation at 976 nm laser. In the present case we have used nanophosphor as host which has several advantages over hosts used earlier. The upconverting nanophosphor has been synthesized using the solution combustion technique. Samples are structurally and optically characterized using XRD, Raman and FTIR techniques. Factors affecting the multicolored and white emissions such as relative concentration of REs, excitation powers as well as the annealing temperatures are thoroughly investigated in this article.

Experimental Details

Synthesis of $Tm^{3+}/Er^{3+}/Yb^{3+}$:Y_2O_3 Nanocrystalline Phosphor

The yttrium oxide phosphor samples were synthesized through the combustion route using urea as an organic fuel. A detail of the preparation method is described in our earlier work [17]. The compositions of the materials used are

$$(100 - x - y - z)Y_2O_3 + xEr_2O_3 + yYb_2O_3 + zTm_2O_3$$

where x=0.07, 0.15, 0.30 mol%, y=2.5 mol% and z= 0.5 mol%.

The as-synthesized samples were annealed at two different temperatures 800 °C and 1400 °C for 4 h.

Characterizations

X-ray diffraction (XRD) patterns of the samples were recorded using an 18 kW rotating anode (Cu) based Regaku powder diffractometer fitted with a graphite monochromator and the average size of the crystallites was estimated from these studies. Fourier transform infrared (FTIR) spectra of samples was recorded using Spectrum RX-I spectrophotometer (Perkin Elmer). Similarly the Raman spectra of the samples were recorded using WITEC alpha 300 confocal Raman system equipped with a Nd:YAG laser (532 nm) as the excitation source. The UC luminescence measurements were carried out by exciting the samples with 976 nm radiation from a diode laser and recorded using iHR320, Horiba Jobin Yvon, spectrometer.

Results and Discussion

Structural Features and Analysis

XRD Study

Thermal analysis of as-synthesized sample suggests that it will be interesting to study the as-synthesized sample and the samples annealed at different temperatures. The samples were annealed at 800 °C and 1400 °C for 4 h. The XRD patterns of all the three samples were monitored under the same experimental conditions. The phase composition, crystallization and the average crystallite size of $Tm^{3+}/Er^{3+}/Yb^{3+}$:Y_2O_3 phosphors were analyzed by the XRD patterns. Figure 1 shows the XRD patterns of the as-synthesized and samples annealed at different temperatures.

The XRD pattern of the samples match well with the characteristic peaks of the standard cubic Y_2O_3 structure (JCPDS no. 41–1105) which belongs to *Ia3* (206) space group with lattice parameter a=1.06041 nm. The identical diffraction patterns in Fig. 1 confirm the presence of single cubic crystalline phase of Y_2O_3 even in the as-synthesized sample. The XRD peaks become narrower on annealing the samples at higher temperatures. The RE doping has no effect on the Y_2O_3 phase as is evident from XRD patterns. The average crystallite size of the samples calculated using Debye-Scherrer formula for the as-synthesized and samples annealed at 800°C and 1400°C were found to be 9, 26 and 46 nm respectively. This indicates that annealing at higher temperature enhances the average crystallite size.

Optical Characterizations

Fourier Transform Infrared (FTIR) analysis

FTIR spectra for the as-synthesized and the annealed samples of $Tm^{3+}/Er^{3+}/Yb^{3+}$:Y_2O_3 at 800 °C and 1400 °C are shown in Fig. 2. The absorption peaks in the region 450–570 cm^{-1} are the characteristic stretching vibrations of Y-O in Y_2O_3 structure. The distinct peak around 1390 cm^{-1} is originated due to NO group present in the sample. Also, the peaks in the range 1500–1660 cm^{-1} can be attributed to

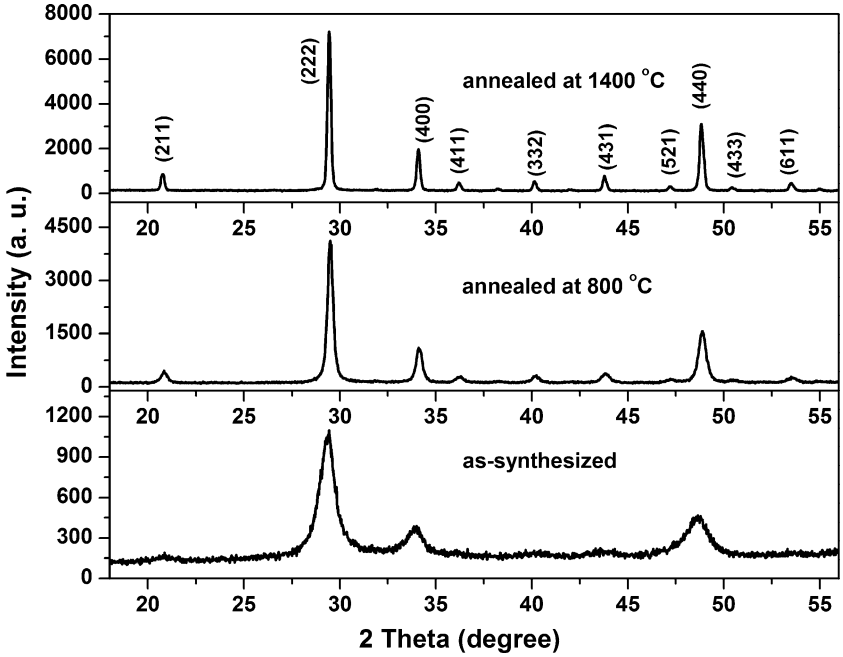

Fig. 1 X-ray diffraction patterns of as-synthesized as well as annealed $Tm^{3+}/Er^{3+}/Yb^{3+}$: Y_2O_3 nanophosphors at 800 °C and 1400 °C temperatures for 4 h

the water molecule while the peaks around 2358 cm^{-1} could be due to CO group present in the powder. A broad peak centered at 3584 cm^{-1} corresponds to the stretching vibration of OH group [18]. These groups quench the fluorescence intensity of the sample. From the FTIR spectra it could be easily seen that the intensity of the OH or CO absorption bands is reduced considerably in the sample annealed at 1400 °C. This implies that this sample must show higher luminescent intensity compared to the other two samples containing large number of quenching centers. We observe exactly the same in the spectrum as said.

Raman Spectroscopy

Figure 3 displays the Raman spectra (λ_{ex}=532 nm) of as-synthesized as well as annealed $Tm^{3+}/Er^{3+}/Yb^{3+}$:Y_2O_3 phosphors at 800 °C and 1400 °C recorded at room temperature under the same experimental conditions. Yttrium oxide is characterized by a very strong Raman band at 377 cm^{-1}. A relatively large intensity of this band indicates a large polarisability variation during the vibration. There are large number of other peaks also present in the Raman spectra particularly in the sample annealed at 800 °C.

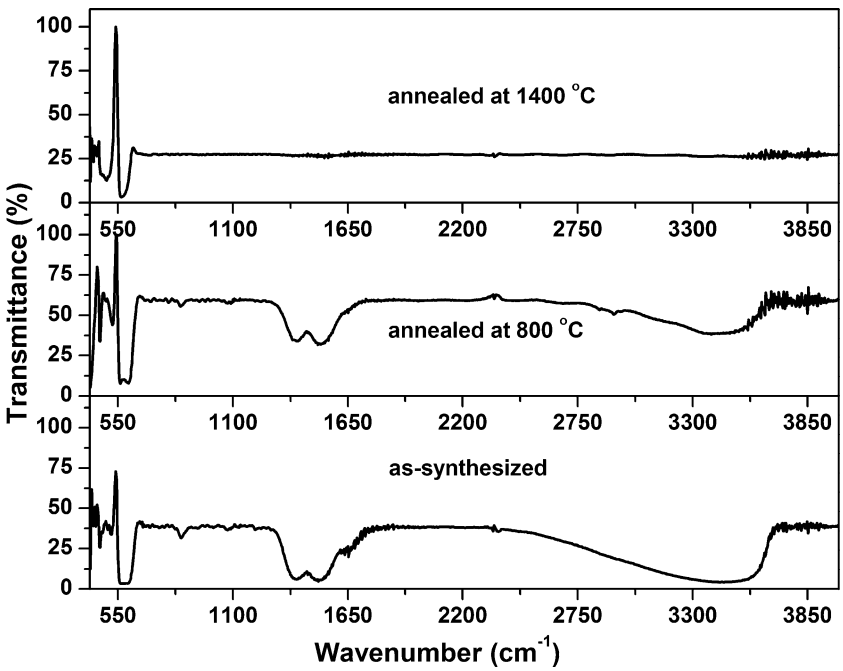

Fig. 2 Fourier Transform—Infrared transmission spectra of $Tm^{3+}/Er^{3+}/Yb^{3+}$:Y_2O_3 nanophosphors **a** as-synthesized **b** annealed at 800 °C and **c** annealed at 1400 °C for 4 h

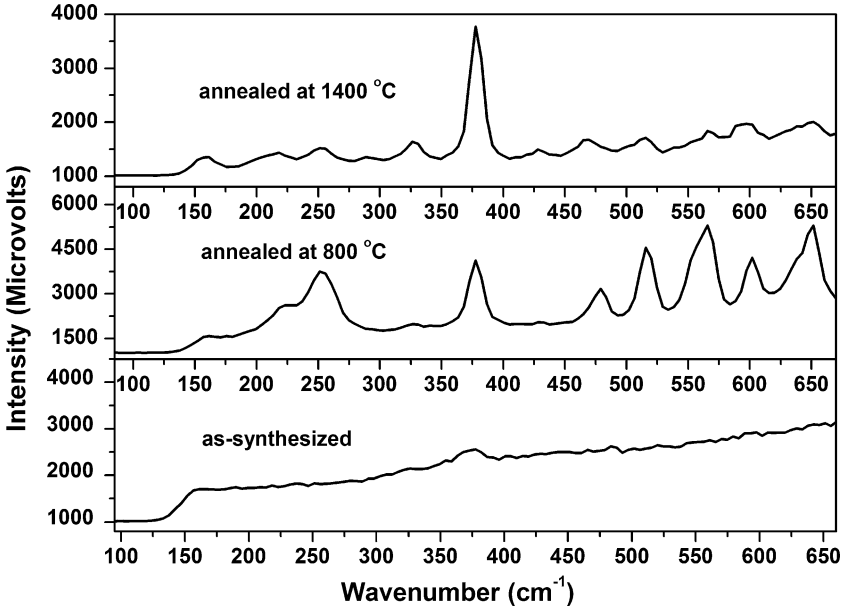

Fig. 3 Raman spectra of Tm^{3+}/Er^{3+}/Yb^{3+}:Y_2O_3 nanophosphors **a** as-synthesized, **b** annealed at 800 °C and **c** annealed at 1400 °C for 4 h

The CO and OH groups must still exist in the as-synthesized sample. These results are in fair agreement with reports on Raman spectrum of Y_2O_3 [19–21]. In the present case we have calculated the band width of strongest Raman peak at 377 cm^{-1} for all the samples. It has been found that band width decreases with the increase in annealing temperature (17.41, 11.16 and 10.5 cm^{-1} for as-synthesized, annealed at 800 °C and 1400 °C respectively). It could be possible that local stress and a large number of point defects can lead to a local lowering of symmetry and to the broadening of the band in the as-synthesized sample [22]. The bandwidth decreases with the increase in the size of the scattering centers. Thus Raman characterization supports the increase in crystallite size on annealing as observed by XRD. Such behavior was also reported by other groups in Y_2O_3 [23].

Upconversion Mechanism

Figure 4 shows the upconverted emission spectra of Tm^{3+}/Yb^{3+}, Er^{3+}/$Yb^{3+}$and Tm^{3+}/Er^{3+}/Yb^{3+} co-doped Y_2O_3 in 450–750 nm region. For Tm^{3+}/Yb^{3+}co-doped Y_2O_3 nanophosphor, intense blue and relatively weak red emission peaks centered at 478 nm and 658 nm are observed. They are attributed to $^1G_4 \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3F_4$ transitions in

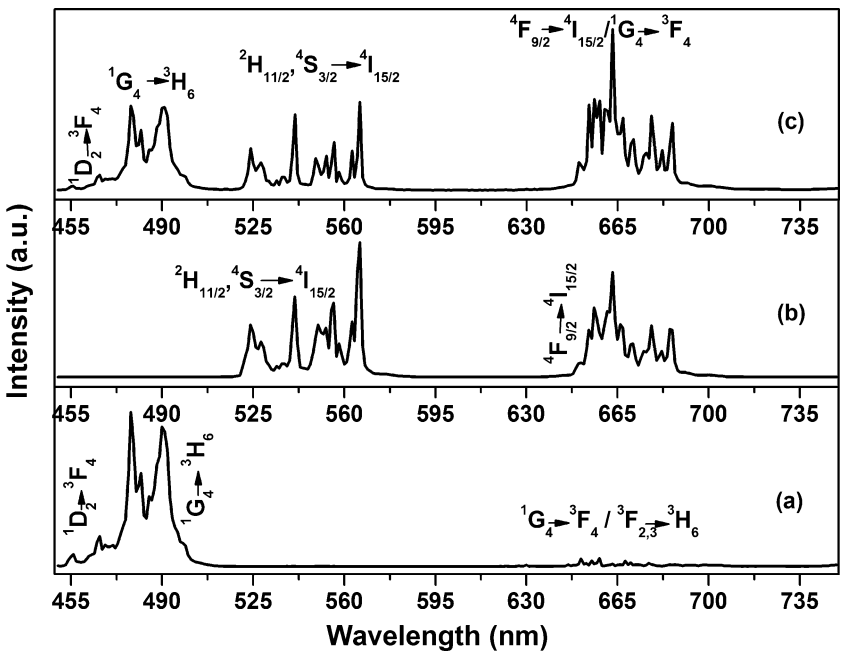

Fig. 4 Room temperature upconversion emission spectra of **a** Tm^{3+}/Yb^{3+}:Y_2O_3, **b** Er^{3+}/Yb^{3+}:Y_2O_3, and **c** Tm^{3+}/Er^{3+}/Yb^{3+}:Y_2O_3 nanophosphors under 976 nm laser excitation

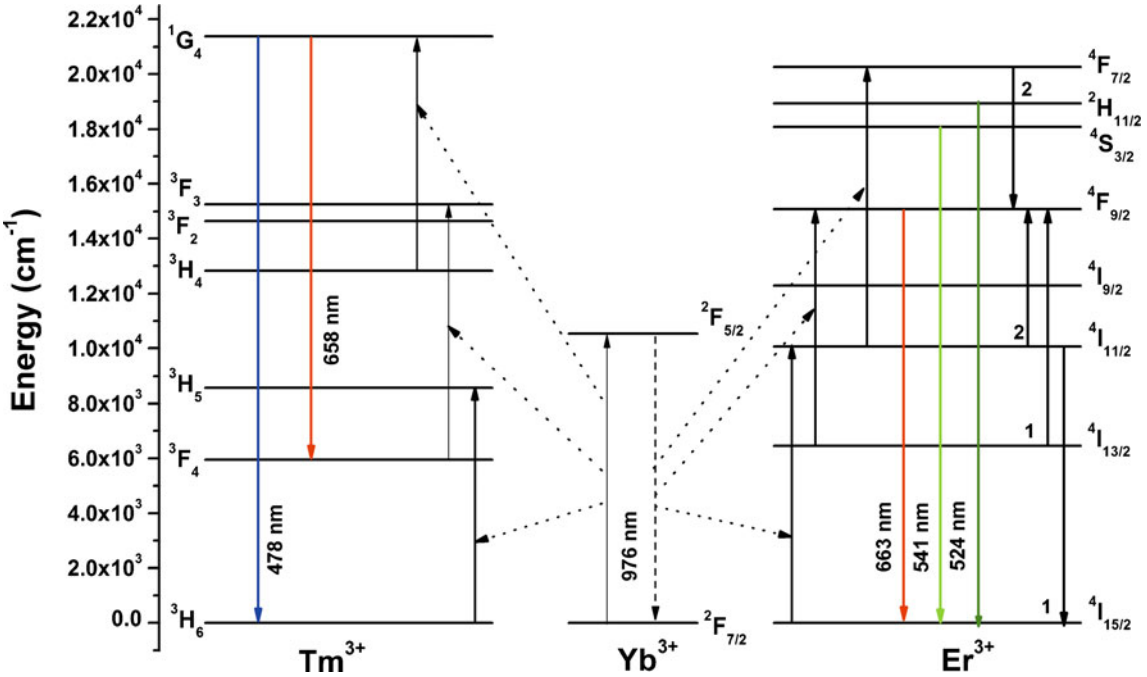

Fig. 5 A schematic energy level diagram for Tm^{3+}, Er^{3+} and Yb^{3+} ions and the different channels responsible for multicolored emission

Tm^{3+} ion respectively. Emissions obtained in UV and NIR regions have been discussed in detail in our previous works [24, 25]. For Er^{3+}/Yb^{3+} co-doped Y_2O_3 nanophosphor, the emission peaks observed at 524 nm and 541 nm are assigned to the ($^2H_{11/2}$, $^4S_{3/2}$) → $^4I_{15/2}$ transitions of the Er^{3+} ion, while the peak observed in the red region at 663 nm is attributed to $^4F_{9/2}$ → $^4I_{15/2}$ transition. In the complex tri-doped system, we observe emission from all the three dopants in red, green and blue regions overall giving white light generation for Tm^{3+}(0.5 mol%)/Er^{3+}(0.3 mol%)/Yb^{3+}(2.5 mol%) doped Y_2O_3 nanophosphor annealed at 1400 °C.

Figure 5 represents a schematic diagram of the energy levels of the three RE ions. The diagram also depicts several energy transfer, cross-relaxation and non-radiative multiphonon mechanisms occurring in Tm^{3+}, Er^{3+} and Yb^{3+} when they are excited with 976 nm radiation. Actually 976 nm laser radiation excites only Yb^{3+} since Tm^{3+} has no level at this energy. Though Er^{3+} ions are excited weakly with 976 nm (due to its low absorption cross-section) but its concentration in the sample is very low compared to Yb^{3+}. It is well known that Yb^{3+} ions can efficiently sensitize Er^{3+} and Tm^{3+} ions [26, 27]. Hence, it

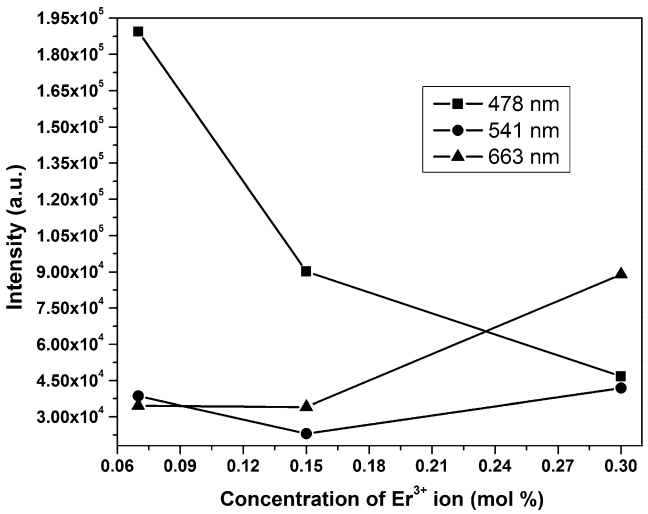

Fig. 6 Change in upconversion emission intensity of $Tm^{3+}/Er^{3+}/Yb^{3+}$:Y_2O_3 nanophosphors with increasing concentration of Er^{3+} ion

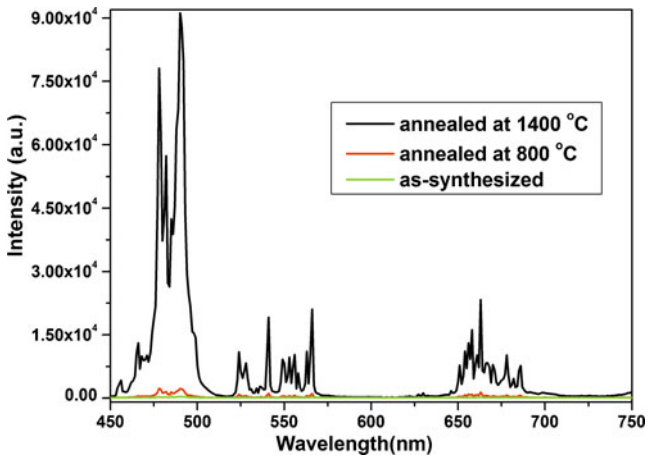

Fig. 7 Upconversion emission spectra of $Tm^{3+}/Er^{3+}/Yb^{3+}$:Y_2O_3 nanophosphors at different annealing temperatures

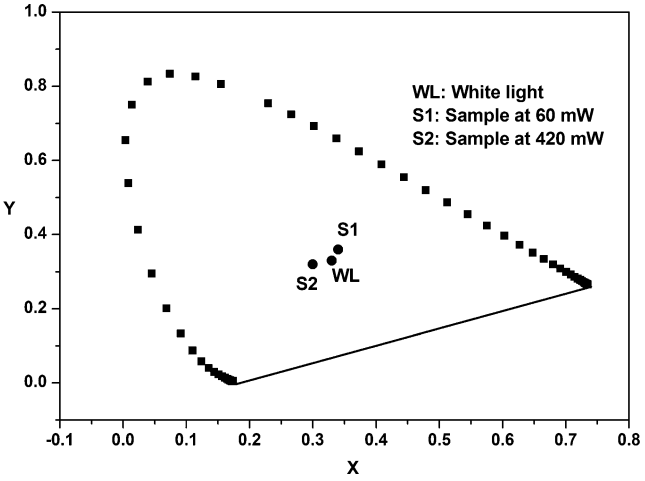

Fig. 8 Color coordinates for white light using 976 nm laser excitations (60 mW and 420 mW) for sample annealed at 1400 °C

is reasonable to believe that the main path to populate the upper emitting levels is the energy transfer from Yb^{3+} to Tm^{3+} and Er^{3+} ions. For Tm^{3+}/Yb^{3+}codoped system, Yb^{3+} ions transfer their excitation energy to Tm^{3+}ions to populate the $^3H_4$, $^3H_5$, $^3F_2$ ($^3F_3$), $^3F_4$ and $^1G_4$ levels through relaxation and reabsorption processes. For the Er^{3+}/Yb^{3+}co-doped system, the $^2H_{11/2}$,$^4S_{3/2}$ and $^4F_{9/2}$ levels are again populated through energy transfer from Yb^{3+} to Er^{3+} ions and have been widely investigated [28, 29]. As has been proposed, the red UC emission of Er^{3+} is highly concentration dependent compared to green one. In the present investigation concentrations of Tm^{3+} and Yb^{3+} were kept fixed at 0.5 mol% and 2.5 mol% respectively whereas that of Er^{3+} was varied as 0.07, 0.15 and 0.30 mol%. Variation in intensity of red, green and blue emissions with Er^{3+} concentration is shown in Fig. 6. For these concentrations intensity ratios of green to red emissions are 1.11, 0.68 and 0.47 for the sample annealed at 1400 °C. This is due to excess population in $^4F_{9/2}$ level (upper level of red transition) at higher concentrations of Er^{3+}. Based on the energy matching conditions and the cross relaxation processes:

$$^4I_{11/2} \rightarrow {}^4I_{15/2} + h\upsilon : {}^4I_{13/2} + h\upsilon \rightarrow {}^4F_{9/2}; \text{ and}$$

$$^4F_{7/2} \rightarrow {}^4F_{9/2} + h\upsilon : {}^4I_{11/2} + h\upsilon \rightarrow {}^4F_{9/2}$$

are the main up-conversion processes in populating $^4F_{9/2}$ level. These processes depopulate the green-emitting $^4S_{3/2}$, $^2H_{11/2}$ levels and populate $^4F_{9/2}$ level, thereby decreasing the green to red ratio (shown as channels 1 and 2 in Fig. 5). Although a very weak contribution to the red emission peak (658 nm) due to the $^1G_4 \rightarrow {}^3F_4$ transition of Tm^{3+} is also likely, it is over shadowed by the strong red emission from Er^{3+} ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) transition. However, in all situations the contribution of Tm^{3+} ions to the red UC band in Fig. 4 (c) is very small and can be neglected due to the following three reasons. Firstly, the intensity of 658 nm band in Fig. 4 (a) is much smaller than that of the blue band. A similar thing is also expected in the tri-doped situation (see Fig. 4 (c)). Secondly, the shape of the red band in Fig. 4(c) is exactly the same as that of Er^{3+} ions in Fig. 4(b) indicating the contribution of Tm^{3+} ion to be negligibly small. Lastly, the pump power dependence of the red in Fig. 4(c) is quadratic which disagree with the cubic dependence for Tm^{3+} ions. In the $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped system Tm^{3+} and Er^{3+} interaction (energy transfer) is very small and can be ignored.

One interesting result is that the luminescence intensity is higher for the sample annealed at higher temperature. The enhancement in intensity is to be ascribed to the removal of the fluorescence quenching centers, e.g. OH, CO etc. An improved crystallinity of samples annealed at higher temperatures also contributes to the enhancement in the emission intensity. Increase in the intensity of all the UC emissions with annealing temperature is shown in Fig. 7.

CIE Diagram

To measure the color of the visible emission that human eye perceives, the Commission internationale de l'e'clairage (CIE) coordinates are calculated and shown in Fig. 8. The CIE-1931 is the standard reference for defining colors and is obtained by considering the sensitivity of human eye to different colors (wavelengths) [30]. In the present work, the color coordinates are calculated with respect to concentration of dopant, annealing temperature and the pump power. The calculated color coordinates vary from (0.16, 0.30) to (0.32, 0.33) providing large scale tunability of multicolored emission. If the concentration of Er^{3+} is changed, it

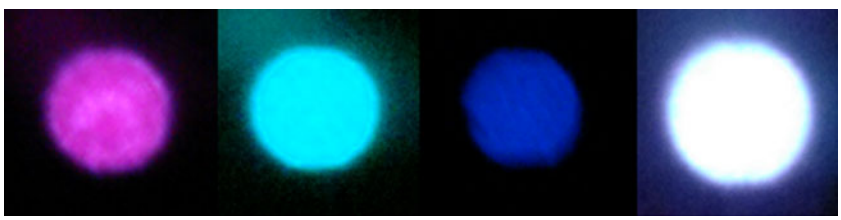

Fig. 9 A digital photograph of the white light from $Tm^{3+}/Er^{3+}/Yb^{3+}$ co-doped Y_2O_3 phosphor and the red, green and blue emissions obtained from the same phosphor using the appropriate color filters

directly affects the color emitted from the sample. As mentioned above, the color coordinates also depend on the annealing temperature. This indicates that particle size also plays a role in defining the color perception. When we increase the pump power the color coordinates shift towards the blue region. This is due to the fact that three-photon process starts dominating to produce additional blue UC emission which is higher than that of the green and red UC emissions.

Also the upconversion efficiency of the $Tm^{3+}/Er^{3+}/Yb^{3+}$:Y_2O_3 nanophosphor has been calculated by taking the intensity ratio between the transmitted visible light and the infrared laser light. The maximum estimated white light efficiency of 2.79% is obtained for the Tm^{3+}(0.5 mol%)/Er^{3+}(0.3 mol%)/Yb^{3+}(2.5 mol%) composition annealed at 1400 °C at the laser power of 420 mW with color coordinates (0.30, 0.32). White emission is observed even at low laser power (60 mW) with color coordinates (0.34, 0.36) (see Fig. 8). Therefore the wide color tunability of white emission with concentration, annealing temperature (crystallite size) and laser power makes it suitable for various optical devices. A digital photograph of sample emitting white light using appropriate filter is shown in Fig. 9.

Conclusions

An efficient tunable white light emission has been observed in $Tm^{3+}/Er^{3+}/Yb^{3+}$:Y_2O_3 nanocrystalline phosphor material synthesized by the solution combustion technique. Upon excitation with 976 nm laser radiation, upconverted blue (from Tm^{3+}), green and red (from Er^{3+}) emissions together result in an intense white emission which is visible to the naked eye even at low laser power (60 mW) with color coordinates (0.34, 0.36). The multicolored emission shows wide tunability with concentration of dopants, the annealing temperature (crystallite size) and the incident laser power. Increase in the emission intensity with annealing temperature is due to the removal of the quenching centers present in the sample. White emission is observed even at low laser power (60 mW) with color coordinates (0.34, 0.36). The maximum upconversion efficiency~2.79% with CIE color coordinates (0.30, 0.32) for Tm^{3+}(0.5 mol%)/Er^{3+}(0.3 mol%)/Yb^{3+}(2.5 mol%) doped Y_2O_3 phosphor annealed at 1400 °C has been obtained with a laser power 420 mW. Provisions for the fine tuning of the multicolored emission to white light with different parameters makes it suitable for various optical devices.

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