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Spectroscopy of lanthanide doped oxide materials: A study of dual-mode luminescence behavior

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Abstract:

The scientific community is now well familiar with luminescent properties of lanthanides. Lanthanide doped oxide phosphors have advantages in terms of sharp and discrete emission lines, metastable energy states, chemical and thermal stability, resistance to photobleaching, non-toxicity, etc. These properties embedded in lanthanide doped oxide phosphors make their study important for different areas of applications, e.g. displays, sensors, solid-state lasers, photovoltaics etc. Lanthanide ions posses ladder like energy levels and hence dual-mode luminescence processes, i.e. downshifting (DS)/photoluminescence (PL) and upconversion (UC), are possible in certain lanthanide doped materials. Dual-mode emission is quite promising for many different applications including bio-imaging and energy harvesting (solar cell). With this concept, the present work is focused on lanthanide (Tb3+, Tb3+-Yb3+) doped oxide nanophosphors synthesized by economically viable solution combustion technique in order to explore the multi-modal emission. The synthesized materials exhibit efficient dual-mode luminescence i.e. discrete emissions in visible region dominated by green one through DS as well as UC process. All these optical processes have been thoroughly explained by the different energy transfer (ET) processes between Tb3+ and Yb3+ ions. In brief, the promising spectral conversion property of the present material is quite useful for displays and next generation solar cells, etc.

Keywords: Lanthanides, Y2O3, Upconversion, Dual-mode luminescence

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1.0 Introduction

Lanthanides have revolutionized the scientific community with its unique optical, magnetic and electrical properties since many decades. Lanthanide activated materials have wide applications in many areas, such as displays, lighting, lasers, light emitting diodes, sensors, optical fibers, security applications, optical data storage, biological applications, solar energy converter and many more. The most important examples are Eu$^{3+}$- activated Y$_2$O$_3$ phosphors, Nd$^{3+}$:Y$_3$Al$_5$O$_{12}$ lasers and Er$^{3+}$ activated optical fibers. Therefore, a rigorous research is going on in the field of lanthanide activated materials [1-6].

Lanthanides have electronic configuration [Xe] 4f$^n$5s$^2$5p$^6$ (‘n’ runs from 0 to 14) and are located at the bottom of the periodic table. These are characterized by partially filled 4f orbitals which are shielded by their outer 5s and 5p electrons. Due to this shielding effect, the lanthanide ions have narrow 4f-4f emission lines with high color purity of the emission. In addition, these ions have energy levels of the order of micro- to milliseconds since these 4f-4f transitions are parity forbidden as per the Laporte rule. But, due to the crystal field effect of the host matrix, the Laporte rule becomes partially allowed and 4f-4f radiative transitions are observed. Thus lanthanides with such advantageous radiative properties are promising spectral converters [7, 8].

In general, the lanthanide ions exhibit excellent photoluminescence properties (Stokes emission). Some of the lanthanide ions are very good in luminescence properties in visible region when excited with UV–Blue radiation and found commercial applications such as Eu$^{3+}$:Y$_2$O$_3$ and Nd$^{3+}$:Y$_3$Al$_5$O$_{12}$, etc. Alongwith the normal photoluminescence properties, some of the lanthanide ions exhibit the Upconversion property. Upconversion is an anti-Stokes type of emission. This optical process takes place by the sequential absorption of two or more incident photons via the long-lived excited states of the ion. This process can take place between same types of ions or between different types of ions; by different channels.
such as Excited State Absorption (ESA), Energy Transfer (ET) between two ions, Photon Avalanche, Cooperative Upconversion, etc [9,10]. Lanthanide activated Upconverting materials have enriched the scientific society with new emerging areas, for example, infrared quantum counter detectors, upconverted lasers, temperature sensors, bioimaging, advanced display devices, white light generation, etc[11-14]. Thus, certain lanthanide ions in a suitable host are capable to exhibit the efficient luminescence properties by excitation with UV-Blue as well as NIR radiation. Such properties are called the dual-modal luminescence behavior of the lanthanide activated materials. Such materials are of great importance since these materials can bridge the spectral gap between UV and IR region of electromagnetic spectrum and can be potential candidates for energy harvesting, biological applications [15].

In order to get efficient luminescence properties, the selection of host for the lanthanides plays a crucial role. The host must possess low phonon frequency to avoid non-radiative losses, similar ionic radii with that of the lanthanide ions, etc. Among the oxide phosphors, $Y_2O_3$ is a promising host matrix with low phonon frequency (~ 550 cm$^{-1}$), with almost same ionic radii with lanthanide ions. In $Y_2O_3$ unit cell, there are two different types of substitutional sites for lanthanide ions. These are point-group symmetry $C_2$ (non-inversion symmetry) and $C_{3i}$ (inversion symmetry) in the ratio 3:1. Thus, the trivalent lanthanide ions can be easily doped in this host matrix and efficient radiative properties are observed [16].

Keeping all the points in mind and in order to investigate the dual mode luminescence behavior, authors have selected terbium lanthanide ion. $Tb^{3+}$ ion is of interest because it has relatively simple energy level structure with low-energy states, $^7F_J$ (J=0-6) and excited state $^5D_4$ and is good green emitting ion through UV-Blue excitation (through DS process). But, the observation of UC process is difficult in $Tb^{3+}$ doped materials. This is because of absence of $Tb^{3+}$ energy levels in NIR region. Therefore, another approach has been adopted in the present work in order to obtain UC in $Tb^{3+}$ ion which is thoroughly discussed in the Results
and Discussion Section. In brief, the synthesis and characterization of Tb$^{3+}$ and Tb$^{3+}$ with Yb$^{3+}$ co-doped Y$_2$O$_3$ phosphors have been carried out in order to explore/probe the dual mode luminescence behavior (emission by a single emitter ion activated oxide material through UC and DS). The samples have been synthesized by novel solution combustion technique. The structural characterization shows the single phase of yttrium oxide. UV excitation of the samples gives beautiful green emission. In addition, the material shows the property of upconversion in presence of Yb$^{3+}$ ion under the 976 nm diode laser excitation.

2.0 Experimental Section

2.1 Material Synthesis

For the synthesis of the phosphors, the analytical reagent (AR) grade yttrium oxide (99.99%, Himedia), terbium oxide (99.9%, Alfa Aeasar), ytterbium oxide (99.9%, Loba Chemie), nitric acid (Merck, 99.9%) and urea (Loba Chemie) were taken for the following sample compositions: Y$_{2-x-y}$Tb$_x$Yb$_y$O$_3$ where x=0.01 and y=0.00 and 0.03.

The solution combustion technique has been employed for the synthesis of phosphor [16]. As the name “combustion” implies, here urea acts as a fuel in this synthesis technique. In the first step, the oxides of host (yttrium oxide) as well as dopants (terbium oxide and ytterbium oxide) were dissolved in minimum amount of conc. HNO$_3$ to obtain the corresponding nitrate solutions and then a small amount of de-ionized water was added further. Urea was then added and the whole mixture was stirred. The obtained solution was heated at ~60-80 °C in a beaker for 3 h to remove the excess water, nitrates and other organic impurities. As the water content in the solution is reduced, the solution is changed into a transparent gel. The gel was transferred in an alumina crucible and kept in a closed furnace maintained at a fixed temperature (~650 °C). An auto ignition and burning gives the phosphor material. Finally, foam like product is obtained which can easily be grinded in an agate mortar into fine powder. The fuel and the rare earth ions concentration are varied till one
achieves maximum fluorescence intensity. The groups OH, NO$_3^-$, and CO$_2$ if left in the powder will quench the fluorescence and so a further heat treatment (annealing) is performed to get rid of these quenching centers. The synthesized samples were annealed at 800°C, 1000°C and 1200°C for 4 hours and the best results were found for the sample annealed at 1200 °C/4h. Therefore, further studies have been carried out for the sample annealed at 1200°C/4h. These have been discussed in detail in further sections.

2.2 Material Characterization:

After the synthesis and annealing of the samples, material characterizations were performed with X-ray diffraction, Fourier Transform Infra-red, and Luminescence measurements. Phase identification was carried out using an 18 KW Cu rotating anode based powder diffractometer fitted with curved crystal monochromator in the diffracted beam (Rigaku, Japan). The XRD data were obtained from $2\theta = 10^\circ$ to 80° at a scan rate of 3°/min. The x-ray generator was operated at 40 kV and 150 mA. Fourier transform infrared (FTIR) measurements were carried out on Spectrum 65 spectrophotometer (Perkin Elmer), and the spectra were collected at a resolution of 2 cm$^{-1}$. The downshifting/photoluminescence studies have been carried out using the 355 nm line of Nd:YAG laser (pulsewidth 7 ns, Spitlight 600, Innolas) and recorded using CCD (Ocean Optics QE 65000). The up-conversion emission measurements were carried out by exciting the samples with 976 nm radiation from a diode laser (continuous mode, Model-III 980, Chengchun New Industries optoelectronics tech. Co. Ltd.) with suitable optical arrangements. The UC emission from the sample is collected through an iHR320 (Horiba Jobin Yvon) monochromator equipped with a photomultiplier tube (PMT, R928) interfaced with a computer.
3.0 Results and Discussions

3.1 Structural analysis:

Figure 1 shows the XRD patterns of as-synthesized and annealed Tb$^{3+}$/Yb$^{3+}$ co-doped Y$_2$O$_3$ phosphor. It is clear from both the XRD pattern that the samples are well crystalline. The crystallinity is enhanced and XRD peaks become shaper in the case of the annealed sample. Both the patterns show that only the single phase of Y$_2$O$_3$ is present in the sample and no secondary or impurity phases are present in the samples. Also, there are no peaks corresponding to dopants which suggest that the dopants are successfully substituted at the cation site of Y$_2$O$_3$. The diffraction patterns are well indexed with JCPDS File 41-1105 which belongs to cubic bixbyte Y$_2$O$_3$ structure with Ia-3 (206) space group. The characteristics peaks are centered at $2\theta$ = 29.18°, 48.52°, 57.52° and 33.76° corresponding to (222), (440), (622) and (400) planes, respectively.

The crystallite sizes of the samples were calculated using the well known Scherrer formula [17] by taking the Lorentzian peak fitting of the three most intense peaks centered at $2\theta$ = 29.18°, 48.52° and 57.52° and were found to be ~28 and ~76 for the as-synthesized and annealed samples. Remarkably, the diffraction peaks are broader in as-synthesized sample compared to the sample annealed at 1200°C/4h. This is due to increase in the crystallite size with annealing temperature. As the sample is annealed at 1200°C/4h the diffractions peaks become more intense (intensity count increases) suggesting the better crystallization in the sample. However phase remains the same. Our results with crystallite size calculation using Scherrer formula shows an increase in crystallite size of about 48 nm. The crystallite size was found to be ~28 nm in case of as-synthesized sample while a size of ~76 nm was obtained in the case of the sample annealed at 1200 °C.
Fig. 1. X-ray diffraction (XRD) patterns of as-synthesized and annealed Tb\textsuperscript{3+}/Yb\textsuperscript{3+}: Y\textsubscript{2}O\textsubscript{3} phosphor. The corresponding JCPDS File no. 41-1105 is also given at the bottom.

3.2 FT-IR ANALYSIS

Fig. 2 presents the FT-IR transmission spectra of as-synthesized and annealed at 1200\degree C/4h Y\textsubscript{2}O\textsubscript{3} phosphor samples. The broad absorption bands around 1522 cm\textsuperscript{-1} and 3455 cm\textsuperscript{-1} are assigned to bending (δOH) and stretching (νOH) modes of OH groups, respectively. A broad band around 1371 cm\textsuperscript{-1} originates from the surface-adsorbed nitrate (νNO\textsubscript{3}) group. These groups possess high vibrational frequencies and therefore act as quenching centers for luminescence, if present in the sample [18, 19]. On annealing the sample at higher temperatures these quenching centers reduce to a good extent. Thus the improvement in the
luminescent properties at higher temperatures can be assigned to the reduction of quenching groups.

Fig 2. Fourier Transform Infrared transmission spectra of Tb\(^{3+}/Yb^{3+}:Y_2O_3\) phosphor samples: as-synthesized and annealed at 1200\(^\circ\)C/4h.

On the lower wavenumber side, there are several peaks in the range 400-600 cm\(^{-1}\). These peaks are at 417, 472, 490 and 560 cm\(^{-1}\) and correspond to stretching modes of Y\(_2O_3\) matrix (\(\nu_{YO}\)). Thus, FT-IR further confirms the low vibrational frequency of the Y\(_2O_3\) host matrix which is favorable for luminescence [20]. Since the rate of multiphonon relaxation depends strongly on the highest phonon frequency of the host material [21], if the phonon frequency is low, the multiphonon relaxation will be poor and vice-versa. Thus, the low phonon frequency of Y\(_2O_3\) and removal of quenching centers enhance the luminescence efficiency in the case of annealed sample.
3.3 Study of Dual mode luminescence behavior

As discussed in the INTRODUCTION part, the dual mode luminescence from lanthanide doped oxide materials is nowadays an active field of research from advanced application point of view. Authors have focused to probe this dual mode luminescence in Tb\(^{3+}\) and Tb\(^{3+}/Yb^{3+}\) co-doped Y\(_2\)O\(_3\) nanophosphors using UV (355 nm) and NIR (976 nm) radiation and tried to propose the mechanism for the results obtained.

3.3.1 Downshifting under 355 nm excitation: Photoluminescence Spectroscopy

The room temperature photoluminescence spectrum of Tb\(^{3+}:Y_2O_3\) nanophosphor was recorded using 355 nm laser radiation and is shown in Fig. 3(a). The spectrum exhibits characteristic emission peaks centered at 489, 542, 593 and 622, 663, and 687 nm of Tb\(^{3+}\) ions. These peaks correspond to \(^5\)D\(_4\) → \(^7\)F\(_6\), \(^5\)D\(_4\) → \(^7\)F\(_5\), \(^5\)D\(_4\) → \(^7\)F\(_4\), \(^5\)D\(_4\) → \(^7\)F\(_3\), \(^5\)D\(_4\) → \(^7\)F\(_2\), and \(^5\)D\(_4\) → \(^7\)F\(_1\) transitions. The \(^5\)D\(_4\)→\(^7\)F\(_3\) transition (542 nm) amongst these is the most intense one.

The mechanism for the observed transitions can be explained with the help of energy level diagram of Tb\(^{3+}\) ion (as shown in Fig. 3(b)). Since 355 nm (~28,170 cm\(^{-1}\)) laser photon partially resonates with \(^5\)L\(_{10}\) level (~28,000 cm\(^{-1}\)) of Tb\(^{3+}\) ion, therefore, the ions are promoted to \(^5\)L\(_{10}\) level after absorbing the incident radiation. Thereafter, the non-radiative relaxation of the excited Tb\(^{3+}\) ions relax transfers the population of ions from \(^5\)L\(_{10}\) to \(^5\)D\(_3\) level. The emissions from \(^5\)D\(_3\) level to lower lying states are not visible in the present case. Also, the energy corresponding to \(^5\)D\(_3\)→\(^5\)D\(_4\) is in resonance with that of \(^7\)F\(_6\)→\(^7\)F\(_0\) transition, therefore, the cross relaxation (CR) process might also be possible [22]: \(Tb^{3+}(\ ^5\)D\(_3\)) + \(Tb^{3+}(\ ^7\)F\(_6\)) → \(Tb^{3+}(\ ^5\)D\(_4\)) + \(Tb^{3+}(\ ^7\)F\(_0\)). In this way, ions in \(^5\)D\(_4\) level finally relax to different low lying levels \([\ ^7\)F\(_J\); \(J = 6, 5, 4, 3, 2, 1]\)] through radiative transition emitting blue, green, red colors.
Fig. 3(a): Photoluminescence spectrum of Tb\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} on excitation with 355 nm showing different transitions of Tb\textsuperscript{3+} ions emanating from $^{5}D_{4}$ level. Inset shows the CIE chromaticity diagram with the calculated color co-ordinates for the emission under 355 nm excitation. (b) Energy level diagram showing the proposed mechanism for the observed emissions from Tb\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} under 355 nm excitation.

CIE chromaticity diagram is a two-dimensional mathematically defined color co-ordinate diagram which gives the visualization of color purity of the emission from luminescent material [23]. The chromaticity color co-ordinates for a particular color (in the visible region) are calculated from the luminescence emission spectra. For the present work, the calculated color co-ordinates for the green emission under 355 nm excitation is found to be (0.34, 0.53) which lie in the green region of the CIE chromaticity diagram as shown in the inset to Fig. 3(a). Thus, CIE chromaticity diagram further confirms that Tb\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} nanophosphor is a promising green emitting material under UV excitation.
3.3.2 Upconversion under 976 nm excitation: NIR to Visible emission through Cooperative sensitization effect of Yb$^{3+}$ ion

UC property in Tb$^{3+}$:Y$_2$O$_3$ nanophosphor under 976 nm excitation has also been investigated in the present work. However, Tb$^{3+}$:Y$_2$O$_3$ nanophosphor does not show any emission under 976 nm excitation. The reason for this may be due to the absence of an energy level in close matching with 976 nm radiation. Therefore, a sensitizer is needed which has energy levels in close matching with 976 nm radiation and also can efficiently transfer its excitation energy to the acceptor ion. These requirements can easily be met by Yb$^{3+}$ ion and is a well known sensitizer for many lanthanide ions [16].

The emission spectrum of Tb$^{3+}$/Yb$^{3+}$: Y$_2$O$_3$ nanophosphor was recorded at room temperature in the range 400-700 nm on excitation with 976 nm radiation and shown in Fig. 4. The spectrum shows several characteristic peaks of Tb$^{3+}$ ion in the visible region dominated by green emission with relatively weak blue and red emissions (as in case of DS under 355 nm excitation, section 3.3.1). These peaks are centered at 488 nm ($^5D_4 \rightarrow ^7F_6$), 542 nm ($^5D_4 \rightarrow ^7F_5$), 590 nm ($^5D_4 \rightarrow ^7F_4$) and 623 nm ($^5D_4 \rightarrow ^7F_3$), 665 nm ($^5D_4 \rightarrow ^7F_2$) and 685 nm ($^5D_4 \rightarrow ^7F_1$).

The 976 nm radiation does not excite Tb$^{3+}$ ion directly (there is no level at this energy) and the presence of Yb$^{3+}$ ions play important role as a mediator which not only has strong absorption for 976 nm but also the energy of photon of cooperative emission from Yb$^{3+}$ match with the energy of $^5D_4$ level of Tb$^{3+}$ ion. Further, the CIE chromaticity diagram for upconversion emission with $\lambda_{exc}$=976 nm is shown in inset to Fig. 4. The calculated color co-ordinates are (0.34, 0.52) which is in the green region of the CIE diagram.
Fig. 4. Room temperature NIR to Visible upconversion (UC) spectrum of Tb$^{3+}$/Yb$^{3+}$: Y$_2$O$_3$ phosphors under $\lambda_{\text{exc}}$=976 nm.

Fig. 5 shows a partial energy level diagram and the mechanism to understand the observed emission through UC process. It is clear that there is no energy level of Tb$^{3+}$ ion in resonance with 976 nm and Yb$^{3+}$ ion has large absorption cross-section ($^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$) for 976 nm radiation. Interestingly, the lifetime of the upper level is found to be of the order of microsecond (half of the lifetime of $^{2}F_{5/2}$ level of Yb$^{3+}$ ion). The first excited state of Yb$^{3+}$ is located at $\sim$10,000 cm$^{-1}$ whereas $^{5}D_{4}$ level of Tb$^{3+}$ ion lies at $\sim$ 20,000 cm$^{-1}$. Therefore, it is proposed that the Yb$^{3+}$ ions transfer energy to $^{5}D_{4}$ level of Tb$^{3+}$ ions through the cooperative sensitization (CET) process [24]. This process involves the simultaneous absorption of two NIR photons by two Yb$^{3+}$ ions and subsequently the simultaneous energy transfer from the Yb$^{3+}$ to a close Tb$^{3+}$: $2\text{Yb}^{3+} (^{2}F_{7/2}) + \text{Tb}^{3+} (^{7}F_{6}) \rightarrow \text{Yb}^{3+} (^{2}F_{5/2}) + \text{Tb}^{3+} (^{5}D_{4})$ as shown in Fig. 5.
**Fig. 5.** The schematic energy level diagram explaining the UC mechanism and the possible Co-operative Energy Transfer (CET) pathways under $\lambda_{\text{ex}}=976$ nm.

### 4.0 Conclusions

In this work Tb$^{3+}$:Y$_2$O$_3$ and Tb$^{3+}$/Yb$^{3+}$: Y$_2$O$_3$ nano-phosphors have been synthesized using simple and economical ‘solution combustion’ technique. The structural characterization shows the single and cubic phase of the phosphor with good crystallinity without any impurity peaks. The crystallinity and particle size are found to increase as the samples are post annealed. In addition, FTIR measurement showed that the optical quenching centers are reduced with post-annealing, due to which a significant enhancement in fluorescence is observed. The material possesses dual mode green emission, i.e. downshifting (DS) and upconversion (UC) on UV and NIR excitations, respectively. All these optical processes have been thoroughly explained by the different energy transfer (ET) processes between Tb$^{3+}$ and Yb$^{3+}$ ions. Therefore, the promising spectral conversion property of the present material is quite useful for displays and next generation solar cells, etc.
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