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## Host Sensitized Luminescence and Time-Resolved Spectroscopy of $\text{YVO}_4\text{:Ho}^{3+}$ Nanocrystals

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### Abstract

Rare earth doped phosphors have attracted much interest because of their high chemical durability and wide range of attractive applications. In this work,  $\text{Ho}^{3+}$  doped tetragonal  $\text{YVO}_4$  nanocrystals have been synthesized via a facile co-precipitation method. The phosphor was characterized by various methods including X-ray diffraction, photoluminescence, cathodoluminescence, time-resolved spectroscopy measurements. The frequency upconversion emission in the synthesized phosphor has been investigated under 800 nm laser excitation. UV-excited photoluminescence (PL) and cathodoluminescence (CL) measurements were performed at room temperature (300 K). A broad band which arises at  $\sim 370\text{--}600$  nm is attributed to the relaxation of  $\text{VO}_4^{3-}$  groups from conduction band to valence band. Under UV-excitation, the presence of a sharp band at 550 nm due to the intra-4f transitions of the trivalent holmium ions suggests energy transfer from  $\text{YVO}_4$  host to RE ions. Luminescence measurements show that this material is suitable for field emission displays (FED) and fluorescent lamps. Also the conversion of UV radiation as well as IR radiation into the visible region suggests the application of this material for photon harvesting in solar cells.

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## 1. Introduction

Recently, rare earth doped inorganic nanomaterials are extensively investigated due to their potential applications in flat-panel displays, light-emitting diodes, optical sensors, bio-imaging systems, solar cell spectrum harvesting, DNA detection and photodynamic therapy [Gu et al., 2013; Huang et al., 2013; Singh et al., 2012; Mahata et al., 2013]. With the development of nanotechnology with nanometer dimension- a major interest has been noticed to control the intrinsic luminescence emission properties of the existing materials by changing their dimension which are essential to meet their technological requirements. It was observed that the crystalline structure, particle shape, size, doping concentration and presence of impurity could modify the performance of rare earth doped nanomaterials [Xu et al., 2010; Zhang et al., 2008].

In rare earth ions, the intra-4f dipole transitions become partially allowed when intermixing of f-states with higher electronic configurations are possible by the local coulomb field of host matrix. The  $\text{YVO}_4$  is an excellent host matrix for rare earth doping due to its mechanical, optical and thermal properties which constitute this material a challenging candidate for photonic and biomedical applications. For an efficient luminescent material, the host should have low phonon energy. The  $\text{YVO}_4$  lattice has maximum phonon energy of  $880\text{ cm}^{-1}$  [Miller et al. 1968] and shows high luminescence efficiency when it is doped with RE ions. It has a zircon type structure, presented by the general formula  $\text{A}^{+m}\text{B}^{+(8-n)}\text{O}_4$ , where A, B are metal ions having co-ordination numbers of eight and four, respectively [Miller et al. 1968]. The zircon type  $\text{YVO}_4$  is built from the chains of alternating edge sharing of  $\text{VO}_4$  and  $\text{YO}_8$ . The  $\text{YVO}_4$  tetragonal crystal belongs to  $\text{D}_{4h}$  space group, with  $\text{D}_{2d}$  local point symmetry of trivalent yttrium ion and is surrounded by eight oxygen ions at the vertices of a tetragonal dodecahedron [Mahata et al., 2015]. The ionic radius of  $\text{Ho}^{3+}$  ( $0.894\text{ \AA}$ ) is nearly equal to that of  $\text{Y}^{3+}$  ( $0.90\text{ \AA}$ ). So the  $\text{Y}^{3+}$  in the  $\text{D}_{2d}$  site of  $\text{YVO}_4$  lattice is easily substituted by  $\text{Ho}^{3+}$ .  $\text{Eu}^{3+}$  doped  $\text{YVO}_4$  is a widely known red phosphor. Apart from this, there are few reports where rare earth doped  $\text{YVO}_4$  phosphor have been studied as luminescent material [Hirano et al., 1996; Mahata et al., 2014; Riwotzki et al., 1998].

In rare earth series, trivalent holmium is a suitable ion especially as a NIR-upconverter ion due to its favorable energy levels for sequential multiphoton absorption [Walsh et al., 2005]. Therefore, because of the scarcity of complete studies of  $\text{Ho}^{3+}$  luminescence in vanadate based host materials, we report our study on  $\text{Ho}^{3+}$  activated  $\text{YVO}_4$  nanocrystals characterized by upconversion luminescence, downconversion luminescence, cathodoluminescence and time-resolved spectroscopy.

## 2. Experimental

### 2.1. Synthesis of $\text{YVO}_4$ : $\text{Ho}^{3+}$ nanocrystals

The  $\text{YVO}_4$ :  $\text{Ho}^{3+}$  nanocrystals were prepared by a co-precipitation route reported elsewhere [Mahata et al., 2014]. The composition of the material was - 99.8 mol%  $\text{YVO}_4$  + 0.2 mol%  $\text{Ho}_2\text{O}_3$ . The starting materials viz.  $\text{V}_2\text{O}_5$  (Sigma Aldrich),  $\text{Y}_2\text{O}_3$  (Merck) and  $\text{Ho}_2\text{O}_3$  (Merck) were taken as stoichiometric proportion and dissolved in concentrated nitric acid to prepare their nitrate forms. All these nitrates were mixed in a beaker with double distilled water in order to remove the excess acid and placed on a magnetic stirrer whose hotplate was maintained at  $80\text{ }^\circ\text{C}$ . Citric acid was added as chelating agent for metal ions keeping the molar ratio of metal ions to citric acid at 1:2. After that, ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) was added drop wise under vigorous stirring. The pH of the resulted solution was kept at 8.0. The mixture of these reagents was stirred on a magnetic stirrer maintained at  $80\text{ }^\circ\text{C}$  followed by 1 h ultrasonic agitation for uniform mixing. After 36h, the resulted precipitate was separated by centrifugation, washed with distilled water and ethanol several times and dried at room temperature. The as-obtained powder was heated at  $800\text{ }^\circ\text{C}$  for 3h.

### 2.2. Characterization

The phase purity and structure of the synthesized material were characterized by a Bruker-D8 Advanced X-ray diffractometer monochromatized with  $\text{Cu-K}\alpha$  ( $1.5405\text{ \AA}$ ) radiation source and patterns were recorded over the

angular range  $10^\circ \leq 2\theta \leq 80^\circ$ . The 800 nm light, emitted from a Ti-Sapphire laser, Mira 900-F (Coherent) pumped by 532 nm laser (Verdi G10) was used as excitation source to record UC emission at room temperature in SPEX 1000M spectrometer. The cathodoluminescence spectrum was recorded at 5 keV accelerating voltage under  $\sim 10^{-7}$  Torr pressure (vacuum). The lifetime measurements were carried out on a streak system using 266 nm laser excitation in combination with a pulse picker system.

### 3. Results and Discussion

#### 3.1. XRD study

The XRD pattern (fig. 1) of the powder of  $\text{YVO}_4 \cdot \text{Ho}^{3+}$  was indexed to tetragonal phase of  $\text{YVO}_4$  with a zircon type structure which is exactly in agree with the standard card of tetragonal phase of yttrium orthovanadate (JCPDS 76-1649). Fig. 1 does not show the presence of any impurity. The crystallite size was calculated using the Debye-Scherrer formula and Williamson-Hall equation [Mahata et al., 2014]. The Scherrer formula is given by

$$D = (0.9 \lambda) / (\beta \cos \theta) \quad (1)$$

and the Williamson-Hall equation is

$$(\beta \cos \theta) / (\lambda) = 1/D + (\varepsilon \sin \theta) / (\lambda) \quad (2)$$

where, D is the crystallite size,  $\lambda$  is the wavelength of radiation,  $\beta$  is the full width at half maximum (FWHM) of the diffraction peak,  $\theta$  is the diffraction angle and  $\varepsilon$  is the microstrain present in the sample.

The crystallite size calculated using the Debye-Scherrer equation is found within 14-25 nm while the Williamson-Hall plot gives the value as  $\sim 18$  nm.

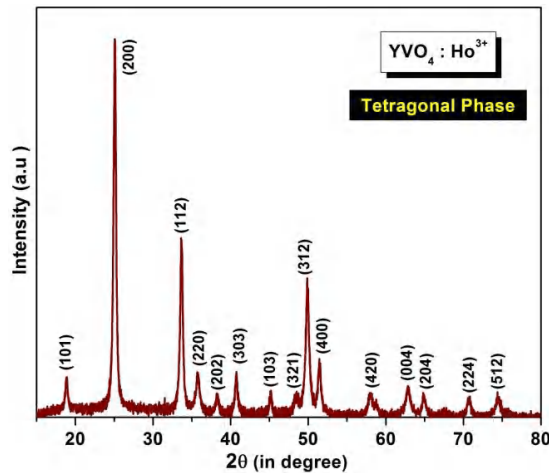


Fig. 1. X-ray diffraction patterns of 0.2 mol%  $\text{Ho}^{3+}$  doped  $\text{YVO}_4$  nanocrystals annealed at  $800^\circ\text{C}$ . The pattern shows tetragonal zircon type structure.

### 3.2. Upconversion emission study

The upconversion emission under 800 nm laser excitation is shown in fig. 2. The four upconversion emission bands were observed between 450 to 800 nm.

The energy level diagram with possible excitation pathways are illustrated in fig. 3. Under 800nm laser excitation, the electron of  $\text{Ho}^{3+}$  ions are raised to  $^5\text{I}_4$  through ground state absorption (GSA) process. From the  $^5\text{I}_4$  level, electrons non-radiatively relax to the  $^5\text{I}_5$  level. The electrons at the  $^5\text{I}_5$  level absorb another incoming photon and rise to the  $^5\text{F}_2$  level. At this time some of the electrons are non-radiatively de-excited to  $^5\text{F}_3$ ,  $^5\text{F}_4$ ,  $^5\text{S}_2$ , and  $^5\text{F}_5$  levels through single phonon or multiphonon processes and produces emission bands at 476, 541, 551, 655 and 755 nm due to  $^5\text{F}_3 \rightarrow ^5\text{I}_8$ ,  $^5\text{F}_4 \rightarrow ^5\text{I}_8$ ,  $^4\text{S}_2 \rightarrow ^5\text{I}_8$ ,  $^5\text{F}_5 \rightarrow ^5\text{I}_8$ , and  $^5\text{F}_4/^5\text{S}_2 \rightarrow ^5\text{I}_7$  transitions respectively. Therefore, all the emission bands are due to two-photon absorption processes lifting the  $\text{Ho}^{3+}$  ion.

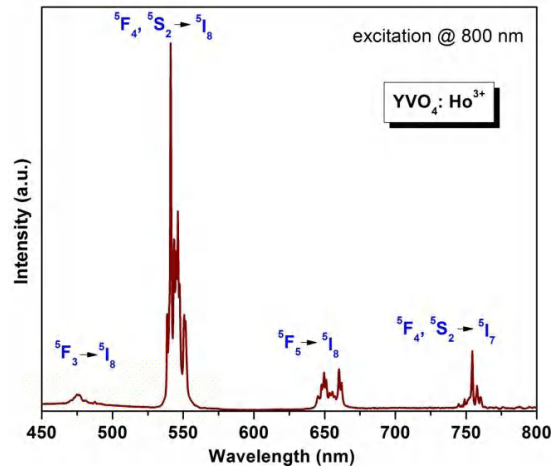


Fig. 2. UC emission spectrum of  $\text{YVO}_4: \text{Ho}^{3+}$  phosphor.

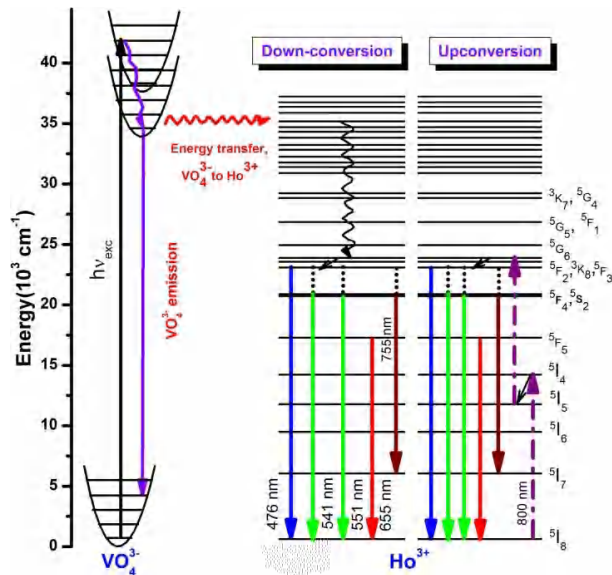


Fig. 3. Energy level diagram with possible transition pathways.

### 3.3. Downconversion emission study

Under 266 nm UV light excitation, a blue emission band in the wavelength range 430-600 nm was observed (fig. 4a). This broad band is attributed to the energy transition of molecular orbital of  $\text{VO}_4^{3-}$  group within  $\text{YVO}_4$ . The other emission bands at 550 nm is from  $\text{Ho}^{3+}$  ions ( $^5\text{F}_4/^5\text{S}_2 \rightarrow ^5\text{I}_8$ ). This reveals the energy transfer from  $\text{VO}_4^{3-}$  groups to  $\text{Ho}^{3+}$  ions. The UV light excites electrons from the filled oxygen 2p levels in the valence band to the empty vanadium 3d levels of the conduction band [Wei et al., 2010]. The excited state then relaxes to the ground state by transferring the energy to the holmium ions.

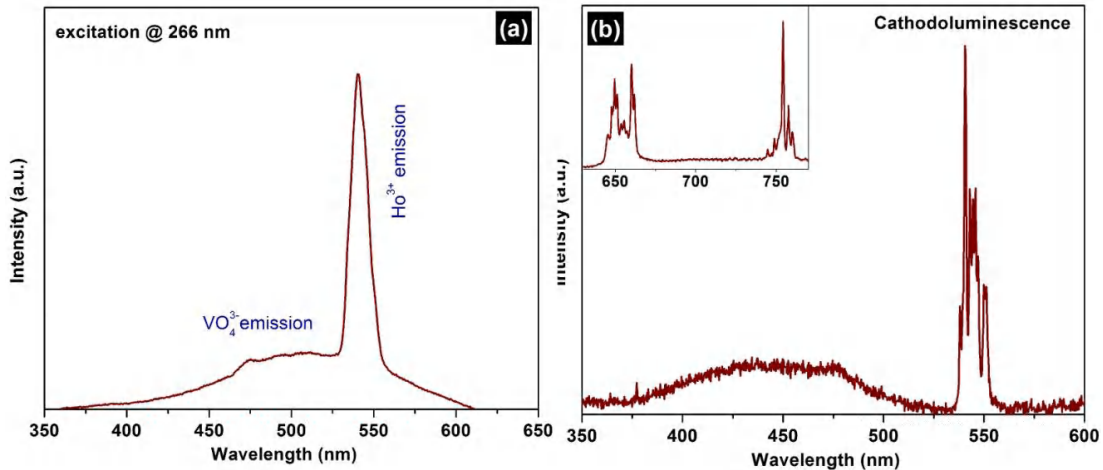


Fig. 4. (a) Downconversion luminescence ( $\lambda_{\text{exc}} = 266$  nm) spectrum of  $\text{Ho}^{3+}$  in  $\text{YVO}_4$  host. As the spectrum was extracted from streak system, the resolution is poor. (b) Cathodoluminescence spectrum of  $\text{YVO}_4:\text{Ho}^{3+}$  phosphor.

### 3.4. Cathodoluminescence study

The development of flat panel displays (field emission displays, plasma display panels, vacuum fluorescent displays, electroluminescent displays, etc.), is still a primary research area [Li et al., 2014]. These emissive displays produce light by excitation of phosphors. To compete with the liquid crystal displays, the phosphors used as flat-panel displays should have good efficiencies to reduce the power consumption. Therefore, the present material was investigated under electron beam excitation; the prepared material exhibits the same type of spectrum as obtained for downconversion photoluminescence (fig. 4a&b). However the relative position of the broad band is shifted from photoluminescence; this may be caused by different excitation processes. The spectrum shows blue broad band emission with characteristic rare earth emission bands.

### 3.5. Time-resolved spectroscopy

The decay time of ( $^5F_4$ ,  $^4S_2$ ),  $^5F_5$  levels have been measured under 266 nm UV light excitation. The decay curves are shown in fig. 5. The feeding of the energy levels population occurs by direct energy transfer from  $VO_4^{3-}$  groups through the higher energy levels by multi-phonon relaxation process. Both the curves were well fitted with single exponential decay function. The decay times of ( $^5F_4$ ,  $^4S_2$ ),  $^5F_5$  levels are measured to be 1.8 and 2  $\mu$ s respectively. However, these measured decay times are shorter in the  $YVO_4$  host in comparison to other host materials [Zhou et al., 2013]. The variation of decay lifetime with different temperature will be explored in future.

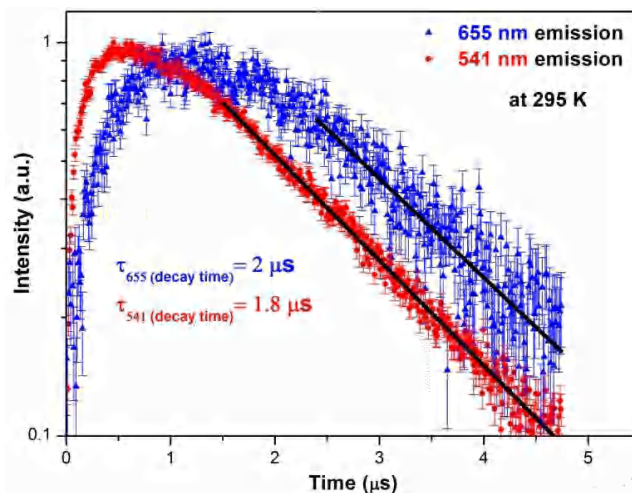


Fig. 5. Measured decay times of ( $^5F_4$ ,  $^4S_2$ ),  $^5F_5$  levels of  $Ho^{3+}$  in  $YVO_4$  host.

#### 4. Conclusions

In summary, we report the luminescence properties of  $Ho^{3+}$  doped  $YVO_4$  nanocrystals prepared by co-precipitation method. The energy transfer from  $O^{2-} - V^{5+}$  charge transfer state to  $Ho^{3+}$  ions is observed. The time-resolved spectroscopy also supports the energy transfer to the  $Ho^{3+}$  ion. This phosphor can effectively convert UV as well as NIR light into visible light. This result has prospect for employing this material in solar cell for solar spectrum harvesting. The cathodoluminescence measurement proves the application of this phosphor in field emission displays.

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