Science Vision 14(3), 112-117

Original Research

2014
July-September
ISSN (print) 0975-6175
ISSN (online) 2229-6026

Spectroscopic studies of Ho^{3+} doped SiO_2-TiO_2 nanoparticle for photonic applications

Suman Rai and Andrew L. Fanai

Laser and Photonics Laboratory, Department of Physics, Mizoram University, Aizawl 796 004, India

Received 26 April 2014 | Revised 20 May 2014 | Accepted 30 May 2014

ABSTRACT

The spectroscopic properties of Ho^{3+} in SiO_2-TiO_2 were investigated using optical absorption and fluorescence studies. The intensities of the electric dipole transitions of Ho^{3+} in the SiO_2-TiO_2 doped glasses were calculated from the absorption spectra in the visible region. From the experimental values of the oscillator strengths and calculated matrix elements, the Judd-Ofelt intensity parameters were calculated by least square analysis. The fluorescence spectral distribution of Ho^{3+} has been recorded using 370nm excitation source. The emission bands observed near blue and green regions were assigned as $^5G_5$, $^5G_6 \rightarrow {}^5I_8$, $^5F_3 \rightarrow {}^5I_8$ and $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ radiative transitions.

Key words: Fluorescence; Judd-Ofelt; oscillator strength; photoluminescence; sol-gel.

INTRODUCTION

Rare earth (RE) doped glasses have gained much interest owing to their attractive optical and physical properties. They have many potential and practical applications in the field of photonics, including solid state lasers and optical amplifiers in fiber optic communications.[1-4] The optical properties of RE ions arise mainly from the transitions between the different $4f^n$ energy states, where n denotes the number of electrons on the 4f subshell.[5] The RE ion in the ground state may be excited to a higher energy state if it absorbs radiation having energy equivalent to the energy difference between the ground state and that particular excited state. Moreover, there is a possibility that the ion in the excited state may relax back to the lower energy levels thereby emitting radiation with energy equivalent to the energy difference between the two levels. This is known as photoluminescence (PL). Due to its favorable energy level structure Ho^{3+} is one of the most attractive candidates for dopant among the RE ions. It shows strong luminescence at various wavelengths including the visible region.[6]

The structure and composition of the host glass is also an important factor as the optical properties of the RE dopant are influenced by

Corresponding author: Rai
Phone: +91-8732853277
E-mail: srai.rai677@gmail.com

their local environment .[7] The properties of the host glass such as density, refractive index, transparency, phonon-energy etc. have immense contribution to the luminescence properties. Silica, though it has high phonon energy, is an attractive host material as a result of its high chemical durability, thermal stability, and wide range of good transparency.[8] Many studies have also shown that the presence of semi-conductor nanoparticles enhance the luminescence properties.[9, 10] In the recent years studies on synthesis, optical properties and applications of rare earth (RE) doped nanomaterials have been attracting much interest. Among these luminescent materials, up conversion (UC) luminescent materials can convert near IR radiation into visible radiation by emitting a higher energy photon after absorbing multiple lower energy photons. In addition, the availability of low-cost near IR diode (980nm) has also stimulated research and applications in the area of UC luminescent materials. Materials doped with Er^{3+} ions posses a favorable metastable energy level with longer lifetime excited states and Yb^{3+} ion have a large absorption cross-section around 980nm and can efficiently transfer the excitation energy to Er^{3+} ions. TiO_2 have attracted much attention in recent years due to its interesting properties and many potential applications such as solar cells, sensors, photo catalysis etc.[11, 12] Many studies have been done on the photonic applications of TiO_2 as waveguides and as thin films.[13, 14]

In this paper, we report the synthesis and optical properties of Ho^{3+} and TiO_2 nanoparticles co-doped in silica glass. The glass samples are prepared by sol-gel technique, which is a low temperature method of synthesis from a liquid phase and allow great control over the concentration of the dopants. The dependence of the luminescence property on the concentration of the TiO_2 is also shown. The optical studies are done by the use of Judd-Ofelt analysis.[15-17]

Experimental

The glass sample was prepared by sol-gel technique where tetraethyl orthosilicate (TEOS) is used as the glass precursor. Methanol was used as the solvent, nitric acid as the catalyst, holmium chloride and titanium isopropoxide (TIPO) as the sources for the Ho^{3+} and TiO_2 dopants respectively. The dopants were mixed with methanol, nitric acid and water and stirred for 30 minutes. To this solution TEOS was added such that the ratio of TEOS, methanol, nitric acid and water is 16:70:4:10. The solution was further stirred for 1 hour till gelation started. Then the gel was put in a plastic caps and allowed to dry. After few days the gel shrunk to about have its size and solidified. Further drying and densification was done by annealing at 500° C.The glass sample obtained has thickness 0.2 cm and refractive index of 1.779.

The absorption spectrum of the prepared glass sample was recorded using Analytik Jena (model Specord 200) spectrophotometer and the photoluminescence (PL) spectra were recorded using iHR320 imaging spectrometer with the excitation wavelength of 370 nm.

Results and Discussions

The absorption spectrum of the prepared sample is given in Figure 1. Absorption peaks were observed at wavelengths of 643, 538, 485, 471, 451 and 417 nm corresponding to the absorption from the ground state $^5I_8$ to the excited states $^5F_5$, $^5S_2$+$^5F_4$, $^5F_3$, $^5F_2$+$^3K_8$, $^5G_6$ and $^5G_5$ respectively. The transitions within the $4f^n$ configuration of rare earth ions were analyzed using the Judd-Ofelt analysis.

According to Judd-Ofelt Theory, the calculated oscillator strength of the electric dipole transition between two states $|l^N SLJ> \rightarrow |l^N S'L'J'>$ can be expressed as[10]

$$f_{cal}^{ed} = \frac{8\pi^2 mc\bar{v}(n^2+2)^2}{3h(2J+1)9n} \cdot \sum_{\lambda=2,4,6} \Omega_\lambda \left|\langle l^N SLJ \| U^{(\lambda)} \| l^N S' L'J' \rangle\right|^2 \quad (1)$$

where m is the mass of electron, c is the ve-

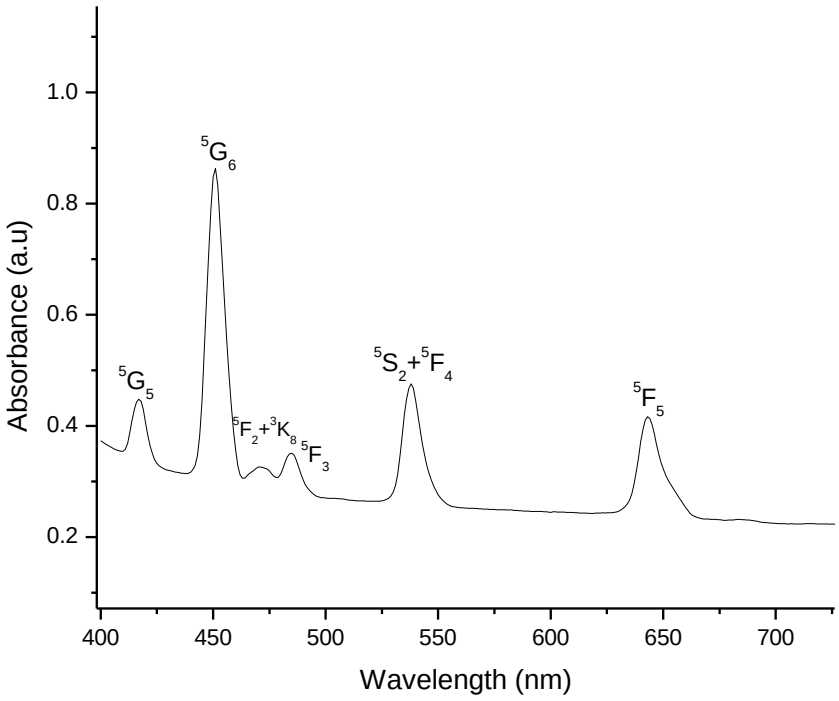

Figure 1. Absorption spectrum of Ho^{3+}:TiO_2-SiO_2 sol-gel glass.

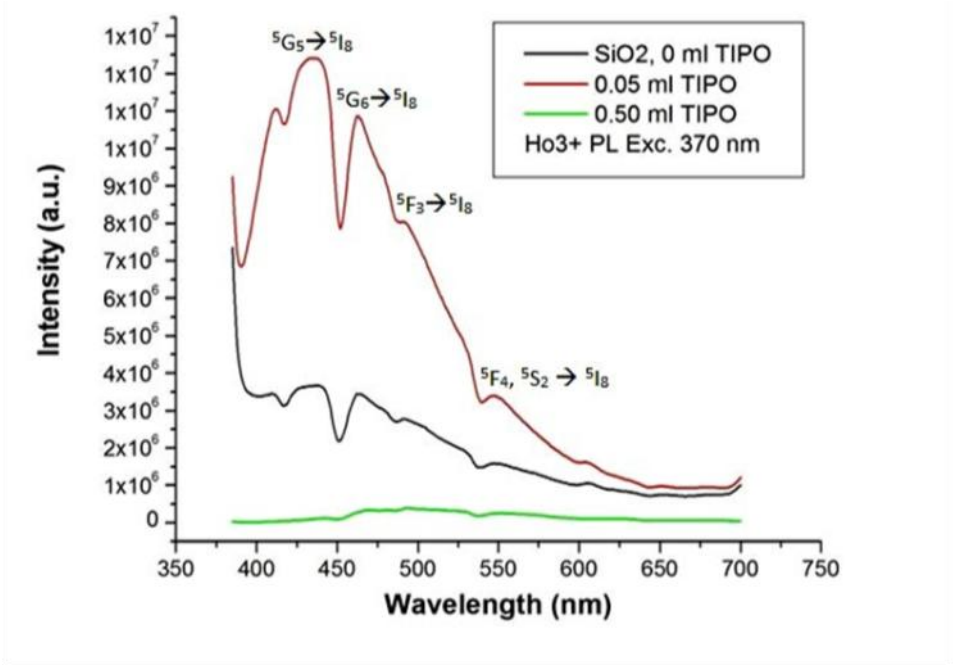

Figure 2. Photoluminescence spectra of Ho^{3+}:TiO_2-SiO_2 sol-gel glass with different concentrations of TiO_2.

locity of light, h is Planck's constant, n is the refractive index, J is the total angular momentum of the initial state, $||U^{(\lambda)}||$ are the reduced matrix elements evaluated in the intermediate coupling approximation for transition $|1^N SLJ> \rightarrow |1^N S'L'J'>$ at energy $\bar{\upsilon}$ expressed in cm^{-1} and Ω_λ are the Judd-Ofelt intensity parameters. The reduced matrix elements $||U^\lambda||$ are known to be relatively host independent, so the values obtained by Carnall *et al.* are used in the calculations.[18]

From the absorption spectrum, the experimental oscillator strengths for transitions from the ground state to the excited states are determined using the relation

$$f_{exp} = 4.318 \times 10^{-9} \int \varepsilon(\bar{\nu}) d\nu \qquad (2)$$

Where $\varepsilon(\bar{\nu})$ is the molar absorptivity at energy $\bar{\upsilon}$ cm^{-1}. The experimentally determined values of oscillator strengths obtained from (2) are co-related with the theoretical expression given in equation (1) and the Judd Ofelt intensity parameters are evaluated using least square fit analysis. The Judd-Ofelt intensity parameters along with the experimental and calculated oscillator strengths are given in Table 1.

The JO intensity parameters give an insight into the local structure and bonding in vicinity rare earth ions.[19] The environment sensitive parameter Ω_2 indicates an amount of covalent bonding and the vibronic dependent parameter Ω_6 is related to the rigidity of the material. The ratio $\Omega_4/\ \Omega_6$- determine the spectroscopic quality of the material. In our sample we have $\Omega_2 > \Omega_4 > \Omega_6$ and $\Omega_4/\ \Omega_6$- = 1.197.

Once the three intensity parameters are known, other useful parameters such as spontaneous transition probability, branching ratio, radiative lifetime etc. can be calculated. The spontaneous electric dipole transition probability between the states $|1^N SLJ>$ and $|1^N S'L'J'>$ is given as

$$A_{ed}(SLJ, S'L'J') = \frac{16\pi^3 e^2}{3h\varepsilon_0 \bar{\lambda}^3 (2J+1)} \frac{n(n^2+2)^2}{9} \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle l^N SLJ \| U^{(\lambda)} \| l^N S' L'J' \rangle \right|^2 \qquad (3)$$

where $\bar{\lambda}$ is the average wavelength of transition.

The fluorescence branching ratio can be calculated from

$$\beta(SLJ, S'L'J') = \frac{A(SLJ, S'L'J')}{\sum_{S'L'J'} A(SLJ, S'L'J')} \qquad (4)$$

where the summation in the denominator is for all the transitions from the excited state $|1^N SLJ>$ to the lower energy states.

The radiative lifetime of an excited state $|1^N SLJ>$ is given as

$$\tau(SLJ) = \left(\sum_{S'L'J'} A(SLJ, S'L'J') \right)^{-1} \qquad (5)$$

Using these equations, the transition probability, branching ratio and radiative lifetime of the various states are calculated and presented in

Table 1. Oscillator strengths and Judd-Ofelt intensity parameters for Ho^{3+}:TiO_2-SiO_2 sol-gel glass.

Transition	Energy (cm^{-1})	f_{exp} ($\times 10^{-6}$)	f_{cal} ($\times 10^{-6}$)
$^5I_8 \rightarrow {}^5G_5$	23981	1.793	1.999
$^5I_8 \rightarrow {}^5G_6$	22173	10.396	10.385
$^5I_8 \rightarrow {}^5F_2 + {}^3K_8$	21231	0.331	1.172
$^5I_8 \rightarrow {}^5F_3$	20619	0.808	0.931
$^5I_8 \rightarrow {}^5F_4 + {}^5S_2$	18587	3.225	2.958
$^5I_8 \rightarrow {}^5F_5$	15552	2.464	2.186
$\Omega_2 = 1.972\times10^{-20}\ cm^2$, $\Omega_4 = 1.469\times10^{-20}\ cm^2$, $\Omega_6 = 1.227\times10^{-20}\ cm^2$			

Table 2. Calculated radiative parameters for Ho^{3+}:TiO_2-SiO_2 sol-gel glass.

Transition		Average Energy (cm^{-1})	A_{ed} (s^{-1})	β	T (μs)
$^5G_5\rightarrow$	$^5I_8$	23041	3265	0.482	147.60
	$^5I_7$	17986	2627	0.388	
	$^5I_6$	14472	630	0.093	
	$^5I_5$	11905	100	0.015	
	$^5I_4$	9839	21	0.003	
	$^5F_5$	7594	132	0.019	
$^5G_6\rightarrow$	$^5I_8$	21692	12883	0.860	66.76
	$^5I_7$	16636	1682	0.112	
	$^5I_6$	13122	181	0.012	
	$^5I_5$	10555	33	0.002	
	$^5I_4$	8489	1	0.000	
	$^5F_5$	6244	200	0.014	
$^5F_3\rightarrow$	$^5I_8$	20408	3321.71	0.816	257.07
	$^5I_7$	15353	339.96	0.084	
	$^5I_6$	11839	246.78	0.061	
	$^5I_5$	9272	132.12	0.032	
	$^5I_4$	7206	22.53	0.006	
	$^5F_5$	4961	6.62	0.001	

Table 2 above.

From the β values in Table 2, we can see that the transitions from the excited levels to the ground state $^5I_8$ are the dominant transitions. The photoluminescence (PL) spectra of Ho^{3+}:TiO_2-SiO_2 glass for different TiO_2 contents is given in Figure 2. The emission bands near 434nm, 461nm and 490nm (blue) are assigned as due to the $^5G_5\rightarrow{}^5I_8$, $^5G_6\rightarrow{}^5I_8$ and $^5F_3\rightarrow{}^5I_8$ optical transitions respectively.[20] The emission bands at green and red comparatively weak compared to blue bands are also observed at 547nm and 620nm correspond to $^5F_4$, $^5S_2\rightarrow{}^5I_8$ and $^5F_5\rightarrow{}^5I_8$ transitions and the radiative parameters are not calculated for these weak transitions. It is observed that the intensity of blue transition $^5G_5\rightarrow{}^5I_8$ is the highest among all the transitions. The TiO_2 concentration is varied by varying the amount of TIPO added in the preparation process.

It is observed that the PL intensity initially increases as the TiO_2 concentration increases, reaches a maximum, and then decreases with further increase in concentration. One possible explanation is that the TiO_2 particles act as network modifiers and increase the concentration of Si dangling and oxygen vacancy in the glass network.[21] In this way, more electrons and holes can be easily excited and radiant recombinations are increased. Moreover, the interesting optical properties of the TiO_2 nanoparticles must be a significant factor. The presence of TiO_2 may assist in the excitation of the RE ions by energy transfer from the TiO_2 particles to the RE ions. The decrease in PL with further increase in concentration may be due to the clustering of TiO_2.

Conclusion

In the conclusion, the absorption and fluorescence spectra for Ho^{3+} in SiO_2-TiO_2 have been investigated. Estimate reveals that the optical parameters are better to that for Ho^{3+} in other glasses reported because of the improvement of the host glass. The ability to use semiconductor nanocrystals as a sensitizer doped with Ho^{3+} ions in SiO_2-TiO_2 glass have been studied. Furthermore, the figures of merit associated with these TiO_2nanocrystals are of sufficient magnitude to quantify this nanocomposite as a high gain material.

Acknowledgement

Authors are thankful to Department of Science and Technology (DST)for financial assistance (no. SR/S2/LOP-0039/2010). One of us, A. Fanai, is also thankful to DST for awarding research fellowship.

References

1. Snitzer E (1961). Optical Maser Action of Nd^{3+} in Barium Crown glass. *Phys Rev Lett*, **7**, 444.
2. Wang SS, Zhou Y, Lam YL, Kam CH, Chan YC & Yao X (1997). Fabrication and characterization of neodymium-doped silica glass by sol-gel process. *Mat Res Innovat*, **1**, 92 –96.
3. Righini GC, ArmelliniC, Berneschi S, Bhaktha SNB, Brenci M, Cacciari I, Chiappini A, Chiasera A, Ferrari M,Jestin Y, Moser E, Nunzi Conti G, Pelli S & Tosello C (2007). Rare-earth-doped silica-based glasses for photonic applications. *J Non-cryst Solids,* **353**, 753–756.
4. Lin H, Jiang S, Jianfeng W, Song F, Peyghambarian N & Pun E (2003). Er^{3+} doped Na_2O-Nb_2O_5-TeO_2 glasses for optical waveguide laser and amplifier. *J Phys D: Appl Phys*, **36**, 812–817.
5. Peacock RD (1975). The Intensities of Lanthanide f↔f Transitions. In: *Rare Earths: Structure and Bonding*. Vol 22, (Eds. Dunitz JD, Hemmerich ZP, Holm RH, Ibers JB, Reinen D & Williams RJP). Springer, Berlin, pp. 84–122.
6. Wang X, Lin H, Yang D, Lin L & Pun E (2007) Optical transitions and upconversion fluorescence in Ho^{3+}/Yb^{3+} doped bismuth tellurite glasses. *J Appl Phys*, **101**, 113535.
7. Van Deun R, Binnemans K, Gorlier-Walrand C & Adam JL (1999). Spectroscopic properties of trivalent samarium ions in glasses. *SPIE*, **3622**, 175–181.
8. Ravi Kumar V, Rami Reddy M & Veeraiah N (1995). Effect of DC Field and X-Ray Irradiation on Dielectric Properties of ZnF_2-PbO-TeO_2 Glasses. *Phys Stat Sol(a)*, **147**, 601–610.
9. Hayakawa T, Selvan ST & Nogami M (2000). Energy transfer between Eu3+ ions and CdS quantum dots in sol -gel derived CdS/SiO2 : Eu3+ Gel. *J Sol-Gel Sci Technol,* **19**, 779–783.
10. Rai S & Bokatial L (2011). Effect of CdS nanoparticles on photoluminescence spectra of Tb^{3+} in sol-gel-derived silica glasses. *Bull Mater Sci*, **34**, 227–231.
11. Eshaghi A, Pakshir M & Mozaffarinia R (2010). Preparation and characterization of TiO_2 sol-gel modified nanocomposite films. *J Sol-Gel Sci Technol*, **55**, 278–284.
12. Akpan UG & Hameed BH (2010). The advancements in sol-gel method of doped-TiO_2photocatalysts. *Appl Catal A*, **375**, 1–11.
13. Bahtat A, Bouazaoui M, Bahtat M & Mugnier J (1994). Fluorescence of Er^{3+} ions in TiO_2 planar waveguides prepared by a sol-gel process. *Opt Commun*, **111**, 55–60.
14. Palomino-Merino R, Conde-Gallardo A, Garcia-Rocha M, Hernandez-Calderon I, Castano V & Rodriguez R (2001). Photoluminescence of TiO_2: Eu^{3+} thin films obtained by sol-gel on Si and Corning glass substrates. *Thin Solid Films*, **401**,1 18–123.
15. Judd BR (1962). Optical absorption intensities of rare-earth ions. *Phys Rev*, **127**, 750–761.
16. Ofelt GS (1962). Intensities of crystal spectra of rare earth ions. *J Chem Phys*, **37**, 511–521.
17. Hehlen MP, Brik MG & Kramer KW (2013). 50th anniversary of the Judd-Ofelt theory: An experimentalist's view of the formalism and its application. *J Lumin*, **136**, 221–239.
18. Carnall WH, Crosswhite H & Crosswhite HM (1978). *Energy level structure and transition probabilities in the spectra of the trivalent lanthanides in LaF_3*. Argonne National Laboratory Report no. ANL-78-XX-95.
19. Dieke GH (1968). *Spectra and Energy Levels of Rare Earth Ions in Crystals*. New York: Interscience.
20. Dutta P & Rai S (2011). Optical transitions and frequency upconversions of Ho^{3+} and Ho^{3+}/Yb^{3+} ions in $Al(NO_3)_3$-SiO_2 sol-gel glasses. *Optik*, **122**, 858–863.
21. Yang P, Song C F, Lu M K, Yin X, Zhou G J, Xu D & Yuan D R (2001). The luminescence of PbS nanoparticles embedded in sol-gel silica glass. *Chem Phys Lett*, **345**, 429–434.